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COKE-OVEN AND BY-PRODUCT WORKS CHEMISTRY

BY

THOS. BIDDULPH-SMITH, F.C.S.
Gold Medallist Coke Oven Managers Association,
Manager and Chief Chemist of the Coke Oven and By Product
Works of Messrs Samuel Fox & Co., Ltd., Stocksbridge

With 62 Illustrations and 7 Folding Plates

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1921

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PREFACE.

It has often been remarked upon, that beyond text-books written and published for the Gas Industry, no books are obtainable for the guidance of the Coke-Oven and By-Product Works Chemist.

The various works on Chemistry applied to Gas Manufacture, although extremely useful, do not by a long way meet his requirements.

I have therefore endeavoured to furnish the Coke Oven and By-Product Works Manager and Chemist with a concise manual, covering, as far as space will allow, the general work required for the Chemical Control of such Plants.

I am indebted to Dr Harold G. Colman and Dr Percy Edwin Spielmann, and also to their respective staffs, for the interest they have taken in the work, and for the valuable assistance they have given in the preparation of the chapters dealing with Benzol Works Tests. Also to Dr G. P. Lishman for assistance in reading over the manuscript, to Mr R. Howson for general assistance and keen interest taken in its production, and to the Society of Chemical Industry and others for permission to reproduce graphs.

THOS. BIDDULPH-SMITH.

COKE-OVEN AND BY-PRODUCT WORKS,
Stocksbridge, *January* 1921

PREFACE TO APPENDIX NO. I.

THE disastrous loss of a large proportion of the Coal Tar Industry from this country to Germany has led to a minute examination of the constituent substances of Coal Tar by the chemists of the latter country; and, incidentally, to a remarkable exhibition of that painstaking, meticulous, and in the main unimaginative character of work which is ordinarily associated with the German chemist. It must be acknowledged that the results obtained by these investigators have been of the greatest value.

It is to be hoped—indeed, it is fully expected—that in the immediate future detailed and difficult work of this kind will be carried on in this country. Our chemists are fully capable of such work; but in order that the best advantage should accrue to the country, there should be the stimulus of insistent demand from the Coal Tar Industry itself for detailed knowledge as to what exactly that industry is handling.

Appendix No. I. has been prepared in order to give a general survey of the nature of the more valuable and also the lesser known substances obtainable by the distillation of coal tar.

References to German literature and patents have been retained, in order to serve as a guide to information which may not otherwise be very readily found. The almost complete omission of references to work done outside Germany is due to the desire that the present information should be circulated without further delay, more especially as British and other work is easily to be traced.

To do the subject justice, a volume should be written on it; but it is hoped that, whilst avoiding too many ordinary "text-book" facts, the information selected will be new to some and of service to many, and that a further and still more incisive interest, both scientific and industrial, will be aroused.

MINISTRY OF MUNITIONS OF WAR,
D.E.S. ANALYTICAL LABORATORY.

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COKE-OVEN AND BY-PRODUCT WORKS CHEMISTRY

CHAPTER I.

WASHERY AND OVENS.

Coal and Coke.

1. **Sampling.**—To sample a large quantity of coal or coke for analysis, perhaps the best method of procedure is to take a shovelful from all parts of the heap, or in the case of charging ovens, from each car-load and throw it into a tub, closed by a lid; grind up the whole to the size of peas as quickly as possible, thoroughly mix, and spread it out in a flat, square heap, divide this diagonally into four quadrants, remove two opposite quadrants, grind the remaining two finer, and repeat the above process until about 10 lbs. of finely ground coal or coke is obtained. The process is again repeated in the laboratory until the fuel passes a 30 mesh sieve, grinding being carried out in this case by means of a porcelain mortar and pestle. Where wet coal is to be tested (*e.g.* coal from washery) the sample as received at the laboratory should be tested direct for moisture, the dried sample then being ground up for the other tests.

2. **Moisture.**—*Coal to which water has been added.*—Heat 100 to 200 grams of coal to 105° C. for two hours, the loss in weight being due to moisture. Prevent a free passage of air over its surface as much as possible. At a higher temperature volatile hydrocarbons would be driven off, thus giving a high result, or if excess of air passes over its surface, oxidation would take place, giving a low result.

Dry Coal and Coke.—Heat 10 grams of the sample, ground fine enough to pass a 30-mesh sieve to 105° C. on a clock glass until a constant weight is obtained. The loss in weight 10 = percentage of moisture.

3. **Volatile Hydrocarbons.**—One gram of the prepared sample is placed in a platinum crucible, at least 1¼" deep, with a tightly fitting lid. The crucible should be heated in a muffle furnace for half a minute after the last traces of escaping hydrocarbons have disappeared. The loss in weight represents on dry coal, the volatile hydrocarbons, and on wet coal, volatile hydrocarbons and moisture.

4. **Fixed Carbon (Coke).**—The residue left in the crucible from the volatile hydrocarbon test represents the fixed carbon and ash, the weight being determined by subtracting the weight of the crucible and lid. Ash is estimated separately, the difference being the fixed carbon.

5. **Ash.**—This estimation is carried out by heating two grams of the coal or coke in silica capsules in the muffle furnace until all the carbon is

burnt away. This can be told by the incandescent appearance of the mass while carbon is still present. Coke requires a much higher temperature than coal. Coal which cakes strongly should be heated up gradually, so that the volatile matters may escape before the powder can form a cake.

6. **Sulphur.**—(*a*) (*Eschka's*) *Method:*—Mix 0·5 to 1 gram of the finely ground coal with 1½ times its weight of an intimate mixture of 2 parts of well burnt magnesia and 1 part of anhydrous sodium carbonate. The mixture is made in a platinum crucible by means of a glass rod, and the crucible is heated, without the lid, in an inclined position in such a manner that only its lower portion attains red heat. The mixture should be frequently stirred up with a piece of platinum wire during combustion, which lasts for about an hour, the colour of the mixture changing from grey to a reddish brown. After cooling, the calcined mass is washed into a beaker with distilled water, and bromine water is added until the liquid shows a light brown colour, then heat the whole to boiling, decant through a filter paper, and wash the residue with hot water. Add hydrochloric acid to the aqueous solution, boil until all the bromine has been removed, and add a solution of barium chloride, drop by drop at boiling point, until the precipitation of barium sulphate is complete. If the magnesia or sodium carbonate are not pure, a "blank" should be carried through on these substances, without the sample, and the amount deducted from the total sulphur found. One part of $BaSO_4$ indicates 0·1373 parts of sulphur. A solution of ammonium acetate added to the boiling solution, after precipitation has been found to make the precipitate grow, facilitating its filtration without endangering the accuracy of the estimation.

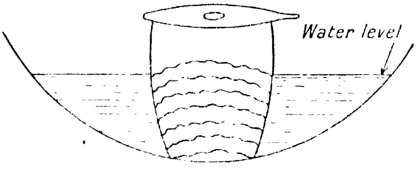

Fig. 1.

(*b*) *Instantaneous Combustion Method.*—Mix 0·7 grams of the fuel with 12 grams of sodium peroxide and 0·5 grams of potassium chlorate in a nickel crucible of about 40·0 c.c. capacity. Stand the crucible in a porcelain dish containing distilled water up to half its height as shown (fig. 1). Ignite the mixture by means of a red-hot wire, through the hole in the lid. When the action is over, wash out the crucible into the dish, add hydrochloric acid until slightly in excess, and then ammonium hydrate until alkaline, filter and wash; add to the filtrate a few drops of methyl orange, and bring to neutral with hydrochloric acid; add 0·5 c.c. HCl in excess; boil, and add barium chloride solution and ammonium acetate solution as before.

A "Blank" should also be carried out with the above method, the combustion of course being unnecessary.

Phosphorus.—Ten grams of coal or coke are ignited in a platinum basin until only the ash is left; this is then fused and digested in a covered beaker with 20 c.c. of brominised hydrochloric acid for an hour at nearly boiling temperature. The bulk of the acid is then removed by evaporation, and the solution is diluted with 30 c.c. of water. The whole is then filtered, and the residue washed with distilled water, 15 c.c. of strong ammonia are added, and this is neutralised by nitric acid from a burette. When no solution takes place, diluted ammonia is added drop by drop until a faint cloudiness or opalescence appears; this is then re-dissolved by addition of a few drops of nitric acid. The liquid is kept near the boiling point during this operation. To the faintly acid solution 3 c.c. of strong nitric acid are added, and then 5 c.c. of a 10 per cent. solution of ammonium molybdate is quickly added, the solution being briskly stirred. After a second or two the yellow ammonium phosphomolybdate settles in a granular form. This is then nearly boiled for five minutes. The precipitate is then filtered off on a tared filter paper, washed with a weak solution of nitric acid, dried on the water bath and weighed; the weight of precipitate × ·163 = per cent. of phosphorus.

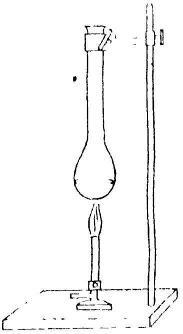

FIG. 2.

The ammonium phosphomolybdate may be estimated in the following manner, which in the author's opinion gives more accurate results.

The precipitate is dissolved in ammonia by placing the filter paper into a beaker containing 5 c.c. ·88 ammonia and about 50 c.c. of water—the beaker in which the precipitation was carried out is usually used. Make the mixture up to 100 c.c. (the true volume of the paper being negligible) and pipette out 50 c.c.—*i.e.* 5 grams of coke, to which add 10 c.c. hydrochloric acid and boil. Add when boiling 10 c.c. of lead acetate solution. Also boil in a second beaker a mixture of 50 c.c. of ammonium acetate solution (obtained by neutralising $33\frac{1}{3}$ per cent acetic acid with ammonia) and 50 c.c. of a 20 per cent. solution of ammonium chloride. Mix the contents of the two beakers by pouring from one to the other four or five times; allow to stand for a few minutes, and filter off the precipitated lead molybdate; wash with hot distilled water until the washings are free from chlorides; ignite at the front of the muffle, cool and weigh. Lead molybdate represents 0·007 times its own weight of phosphorus.

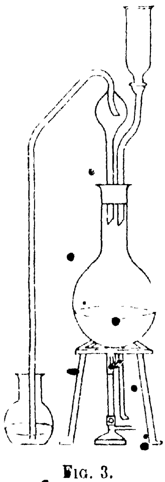

FIG. 3.

7. **Nitrogen.**—Mix 1 gram of the sample with 10 grams of potassium sulphate or persulphate, place in a Kjeldahl's flask, and add 20 c.c. of pure sulphuric acid (free from nitrogen). Digest over a small flame until the black colour has disappeared. (See fig. 2.) Dilute to about 250 c.c., add a small piece of granulated zinc and transfer to the ammonia distillation apparatus (fig. 3), and distil with 250 c.c. of sodium hydrate solution containing approximately 50 grams NaOH, into 20 c.c. of N/10 sulphuric acid.

Each c.c. of N/10 acid used represents ·0014 grams of nitrogen.

8. **Coking Property Tests.**—Dry the roughly ground sample at 100° C., grind fine enough for the whole to pass through a 30-mesh sieve. Weigh into each of six porcelain crucibles 1 gram and add to each different

proportions of silver sand, graded by neglecting the portion not passing a 45-mesh sieve and that passing an 80-mesh sieve. Intimately mix the coal and sand, cover with lids, and roast for 1 hour in a furnace kept at a constant temperature of 450° C. After roasting, turn out the contents of the crucible and examine. If adhering firmly into coke, more sand is needed, and *vice versa*, until the proportion of sand and coal is found, which renders the contents of the crucible, when turned out, to just adhere together and be easily disintegrated with a spatula.

The "Cooking Index" is the percentage of sand in the mixture.

9. Approximate Formula for Calorific Values of Coal.

C = percentage of carbon
V = ,, ,, volatile hydrocarbons.

$$VI = \frac{V \times 100}{C + V}$$

Find A from the following table.

VI	5	10	15	20	25	30	35	38	40
A	115	130	117	109	103	98	94	85	80

Calorific Power.— $= 82C + AV =$ Calories per kilogram
$= (82C + AV)1{\cdot}8 =$ B.Th.Us. per lb.

For estimations of calorific values see "Calorimetry."

Free Coal in Shale from Washery.—200 grams of the shale as taken from the washery are dried and sieved with a 30-mesh sieve. The part not passing through the sieve is placed in a bath of calcium chloride solution of 1·40 specific gravity (for illustration of bath see fig. 4). The particles of coal float on the surface, while the heavier shale sinks to the bottom, where it is caught in a perforated basket. The coal is skimmed off, washed and weighed. Dust is first removed, since the surface tension of the solution holds small particles of stone on the surface, thus giving a higher and inaccurate result.

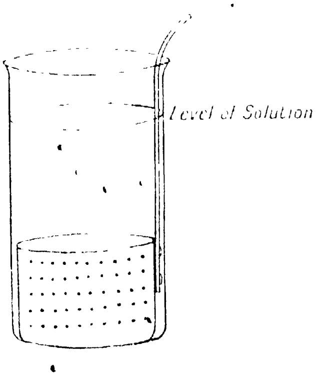

FIG. 4.

Salt in Washery Water.—Where coal containing a high percentage of sodium chloride is treated, the washery water has to be changed when the percentage of salt rises above a fixed figure. This necessitates the periodical testing of the same.

A sample of the water is filtered and 10 c.c. are diluted and titrated with N/10 silver nitrate, using potassium chromate as an indicator, the finishing point being indicated by the red coloration of silver chromate appearing—each c.c. of N/10 silver nitrate solution representing 0·00585 gram of sodium chloride.

CHAPTER II.

GAS.

Estimation of Ammonia.—The opinion of the Author is that there is no method for testing hot moist gas for its ammonia content which can be relied upon. Condensation of the water vapour, and the absorption of ammonia by the condensed water being the most troublesome factor to deal with.

(*a*) Arrange two absorption bottles in series. Into each measure 100 c.c. of 10 per cent. sulphuric acid. Allow the gas to bubble through, measuring

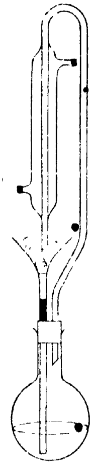

FIG. 5.

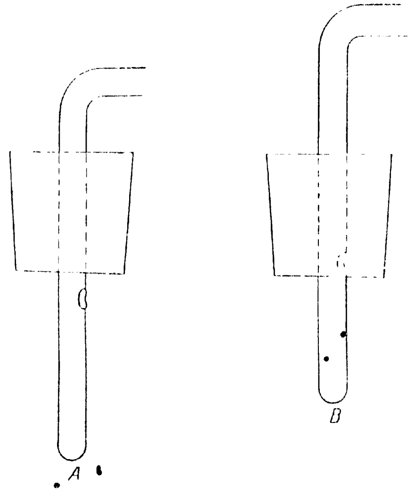

FIG. 6.

it with a meter. 100–200 litres of gas should be passed, the contents of the bottles then being mixed together, and 50 c.c. distilled with excess of caustic soda into 20 c.c. of N/10 sulphuric acid, each c.c. of N/10 acid representing ·0017 gram ammonia.

(*b*) Ammonia is very often estimated by passing the gas direct through the N/10 acid and titrating back. This, however, gives only the free ammonia, the fixed ammonia not entering into the reaction.

Estimation of Tar.—(*a*) 100 litres of gas are passed through two glass towers containing damp cotton wool, and connected together in series. The wool, tar, and condensings are then placed on the funnel of the extraction apparatus shown in fig. 5, the towers being rinsed down with pure benzol, the latter being afterwards placed in the boiling flask. The extraction is carried out by means of the benzol, which afterwards is separated from the condensed water, and evaporated in a weighed flask, the tar remaining behind.

(*b*) When only traces of tar are present the gas is drawn through a weighed sheet of filter paper supported by a wooden frame. The paper is afterwards dried and reweighed.

Estimation of Naphthalene.[1]—150 c.c. of a saturated solution of picric acid in water is placed into a Dreschel's wash bottle; 10 cubic feet of gas is passed at about ½ cubic foot per hour. A precipitate consisting of a mixture of naphthalene and naphthalene picrate is obtained. Without the addition of water, the wash bottle is drained into a round bottom flask, plugged with an india-rubber stopper, through which passes a glass tube sealed at the end, and with a side hole, as shown in fig. 6. Air is extracted from the flask with a suction pump, and by drawing up the tube into position B the flask is sealed. The flask and its contents are then immersed in a water bath, the water boiled until a clear solution is obtained. The whole is allowed to cool, and crystals of naphthalene picrate settle out; filter through a dry filter paper, and titrate 50 c.c. of the filtrate with N/10 sodium hydrate, using lacmoid solution as an indicator; also titrate 50 c.c. of original solution.

Example—

50 c.c. picric acid solution before use	=	20·8 c.c.	N/10 NaOH.
50 ,, ,, ,, ,, after ,,		19·1 ,,	N/10 ,,

1·7 × 3 (for 150 c.c.) = 5·1.
5·1 × 10 (to 100 c. ft.) = 51·0.
1 c.c. N/10 NaOH = ·1975 gram naphthalene.
51 × ·1975 = 10·1 grams $C_{10}H_8$ per 100 c. ft.

Estimation of Cyanogen.—A 30 per cent. solution of caustic soda or caustic potash is mixed with a 12 per cent. solution of ferrous sulphate in the proportion of 5 to 1. The mixture is poured into three Woulfe bottles, and gas is passed through at the rate of 1 cubic foot per hour.

After about 10 cubic feet of gas have been passed, the mixture (collected from the three Woulfe bottles) is washed into a graduated flask, and made up to a definite volume, a portion being taken for analysis; this portion is boiled until free from ammonia, and then filtered. The filter paper is washed with hot water, until a few c.c. of the washings caught in a test-tube, on being acidified with hydrochloric acid, give no blue coloration on the *addition of ferric chloride. The filtrate and washings are acidified with hydrochloric acid, and* ferric chloride is added, the cyanogen being precipitated as "prussian blue." The whole is filtered through a tared filter paper, well washed, dried and weighed.

Example.—10 cubic feet of gas were passed. The mixture of filtrate and washings were made up to 500 c.c., of which 50 c.c. were taken for analysis (= to 1 cubic foot of gas) which produced 1 grains of prussian blue. 860 parts of the latter contain 168 parts of cyanogen, therefore

$$\frac{1 \times 168}{860} = 2·18 \text{ grains of cyanogen per cubic foot of gas, or}$$

$$218 \text{ grains of cyanogen per 100 cubic feet of gas.}$$

---

[1] According to Dr H. G. Colman, *J.S.C.I.*, January 1900.

Estimation of Sulphuretted Hydrogen.—(*a*) *Wanklyn's Method.*—For this test a special bottle (fig. 7) is required. Hold the bottle inverted over the gas supply for 3 minutes. While in this position replace the hollow stopper, which contains caustic soda solution (1·2 specific gravity), shake the bottle for a few minutes, wash all down into the bottle with distilled water, add phenyl phthalein. A colour should be produced showing an excess of caustic soda used, remove alkalinity with hydrochloric acid, dilute, add starch solution, and titrate with N/10 iodine solution, until blue coloration is obtained. Now the bottle is a standard size holding $\frac{1}{10}$ cubic foot of gas, and with this 1 c.c. of N/10 iodine solution = 26 grams sulphuretted hydrogen per 100 cubic feet of gas.

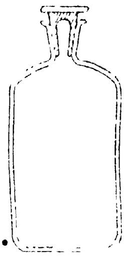

FIG. 7.

(*b*) A solution of ammoniacal sulphate of copper is prepared, of such a strength that 1 c.c. = 0·05 gram of sulphuretted hydrogen. One-tenth of a cubic foot of gas is passed through two Harcourt colour test-tubes, the first of which is charged with a solution of ammonia and distilled water, in the proportion of 1 to 10, and the second with distilled water only, a piece of filter paper soaked in lead acetate solution being placed over the outlet of the second tube, so as to show that the absorption of H_2S is complete. After the gas has passed, the contents of the two tubes are emptied into a white porcelain basin, and titrated with the copper sulphate solution. As the two solutions meet a slight brown tint will appear and the action is complete when the black copper sulphide has separated out, leaving a colourless liquid. The number of c.c. of the copper solution required to effect the *reaction* multiplied by 50 will give the grains of sulphuretted hydrogen per 100 cubic feet of gas.

(*c*) The following method was described by Mr A. B. Way in a paper before the Chemical Section of the American Gas Institute. The apparatus consists principally of a wide mouth bottle of about half a gallon capacity. The neck is fitted with a three-hole rubber stopper, which is marked in any convenient way by means of which one may be sure of its being inserted in the neck of the bottle to exactly the same point each time. Two glass tubes project through the stopper to a distance of about 2 inches above, and to an uneven distance below—one nearly to the bottom of the bottle and the other only a short distance below the stopper. A thermometer is fitted into the third hole, and short, stout rubber tubes with pinch-cocks are attached to the glass tubes. The bottle is calibrated at 60° F., including the tubes, up to the pinch-cocks.

The gas to be examined is passed through the dry bottle until all the air is expelled; and the stop-cocks are then closed—the outlet one first, which ensures a pressure in the bottle. The sample is brought to the laboratory, and allowed to stand until its temperature approaches that of the room; one of the tubes is then connected with a longer rubber tube, the loose end of which is immersed in a beaker holding exactly 1 inch of water; the pinch-cock on this tube is slowly released until the bubbles cease to rise through the water. The gas in the bottle can then be considered at normal pressure. The pinch-cock is then closed and the same tube is connected with a levelling-bottle, the other tube being connected with a large burette containing an ammoniacal solution of cadmium chloride, consisting of 125 c.c. of water, 20 grams of cadmium chloride, and 50 c.c. of strong ammonia, filtered; and 300 c.c. of strong ammonia, made up to 1 litre with water, are added. By means of the levelling bottle a slight vacuum is produced in the sample bottle, and about 30 c.c. of the solution are allowed to run in. The pinch cock is closed and the burette disconnected. The levelling bottle is raised, and at the same time its pinch-cock is opened, the gas which has been drawn out being forced back into the bottle. The levelling bottle is disconnected, and that containing the sample and cadmium chloride solution is shaken for a few minutes. Pressure is slowly released by opening the stop-cock on the shorter tube, the stopper removed, and the contents of the bottle poured on to a dry filter. The bottle is rinsed three times with a little water without attempting to clean out the particles of cadmium sulphide which stick to the bottle and tubes. The precipitate on the filter is washed twice with water, and the filter and precipitate are placed in the bottle. An excess of N/20 iodine solution, 3 c.c. of starch solution, 206 c.c. of water, and 50 c.c. of commercial hydrochloric acid are added. The stopper is inserted, the pinch cocks are closed, and the bottle is shaken for a few minutes. The stopper is again removed, the tubes rinsed into the bottle, and the excess iodine titrated with N/20 thiosulphate solution. By calculation from the calibration of the bottle and the absolute strength of the iodine solution a factor can be obtained which reads directly into grains of sulphuretted hydrogen per 100 cubic feet of gas per cubic centimetre of iodine solution. A correction is made for the temperature, and, if necessary, for the ¼-inch seal. A blank is run through periodically on the reagents employed, and the amount of iodine used in the blank is deducted from the iodine used in the determination. Very accurate results are claimed for this method.

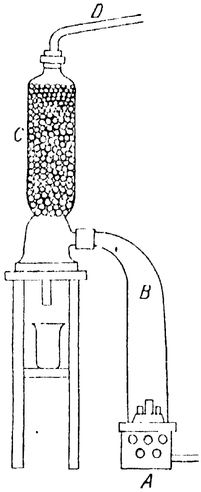

FIG. 8.

Example.—A N/20 solution of iodine contains 6·316 grams of iodine per litre. From the reaction $H_2S + 2I = 2HI + S$ 1 gram of iodine is equivalent to 0·13428 gram of H_2S. Therefore 1 c.c. of N/20 iodine solution = 0·00085214 gram or 0·01315 grain of H_2S. Then—

$$\frac{\text{c.c. in 100 cubic feet}}{\text{c.c. in bottle}} \times 0{\cdot}01315 =$$

grains of H_2S per 100 cubic feet per c.c. of N/20 iodine. Assuming, for instance, that the bottle holds 2000 c.c., we have

$$\frac{5{,}831{,}677}{2000} \times 0{\cdot}01315 = 18{\cdot}618,$$

or 1 c.c. of iodine solution = 18·62 grains of H_2S per 100 cubic feet of gas.

Estimation of Total Sulphur.—(*Referee's sulphur test*).—The apparatus required is shown in fig. 8, and consists of a bunsen burner A, having a steatite tip in which the gas is burned, passing through a short cylindrical stand, provided with a number of holes for the admission of air. The stand has a circular channel on its upper surface for the purpose of receiving the wide end of a trumpet tube B, which is also fitted into a glass tower C, containing glass balls, known as the condenser, and provided at the top with a long glass tube D, which serves as a chimney to create the necessary draught for drawing in air through the holes, and also to find an exit for the incondensable products of combustion. The inlet of the burner is connected to the outlet of an experimental meter, which automatically shuts off the gas when 10 cubic feet have passed. To proceed with a test, surround the stem of the burner with sesquicarbonate of ammonia, light the burner when the index of the meter is at zero, place the trumpet tube in the channel of the burner, and connect the narrow end to the condenser by means of an india-rubber connection, afterwards connecting the long chimney tube to the condenser. The experiment requires fifteen hours for the 10 cubic feet of gas to burn. In the process of burning, the sulphur in the gas combines with the oxygen in the air drawn in through the holes to form sulphurous acid which, combining with the ammonia driven off from the sesquicarbonate of ammonia, forms sulphite of ammonia, this being in turn oxidised to ammonium sulphate, which condenses in the glass tower and is deposited, together with the water resulting from the combustion of the hydrogen in the gas, in the glass beaker placed below the condenser. When 10 cubic feet of gas have been burnt, empty contents of the beaker into a graduated flask. Rinse down with distilled water, the condenser, the trumpet-tube, and the chimney, adding the washings to the measuring flask. Mix the whole of the liquid and divide into two portions: place one portion in a glass beaker covered with a clock glass, and acidify with hydrochloric acid in order to drive off the carbonic acid, raise to boiling point and add an excess of barium chloride solution, and continue to boil for five minutes. Barium sulphate is precipitated, allow to settle, filter, wash until the washings are free from chlorides, ignite in a tared capsule and reweigh. It is advisable to oxidise with bromine before adding the hydrochloric acid.

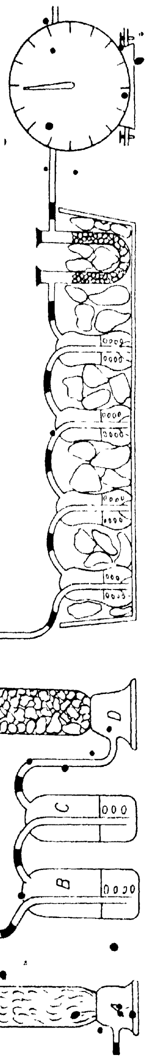

FIG. 9

ESTIMATION OF BENZOL AND ITS HOMOLOGUES.

(d) Müller's Test, or the Increase in Weight of Oleum Petroleum.—*Method.*—The apparatus is fitted up as shown in fig. 9. The gas is led through a glass tower A filled with cotton wool to remove suspended matter, etc., through the two bubbling tubes B and C, containing dilute sulphuric acid and dilute caustic soda solution, for the removal of ammonia, pyridine, phenols, etc., and also through a second glass tower packed with calcium chloride for the removal of moisture. The cleaned gas is then passed through the four weighed absorption bottles filled with oleum petroleum, and the weighed U tube filled with calcium chloride to the meter: the four bottles and the U tube being surrounded with ice. Gas is allowed to pass at the rate of 5 litres per hour, 100 litres being passed. At the expiration of the test the bottles are each disconnected and allowed to stand for twelve hours in order to expel the gas, and the temperature of the four bottles and the U tube allowed to rise to that of the laboratory, being reweighed, and the increase in weight calculated to grams per cubic metre of gas, or by taking the specific gravity of the benzol made on the plant, the results can be calculated to galls. per 10,000 cubic feet of gas. Two sets of apparatus are at work simultaneously, one before the scrubbers and one after them.

Example—

Before Scrubbers. *Gas passed*, 200 *litres.*

	No 1 Bottle	No. 2 Bottle	No 3 Bottle.	No. 4 Bottle.	U Tube.
Weight after test .	92·930	97·768	91·496	104·841	48·938
„ before test .	91·372	96·248	93·221	104·222	47 060
Increase in weight	1·558	1·520	1·275	·619	1 878

Total increase: 6 850 grammes 34·25 grammes per cubic metre.

After Scrubbers. *Gas passed*, 179·61 *litres.*

	No. 1 Bottle.	No. 2 Bottle.	No 3 Bottle	No. 4 Bottle	U Tube.
Weight after test	106 206	96·253	101 432	107 300	60·337
„ before test	105 831	95 821	101 385	107·258	60·228
Increase in weight	·375	·429	·047	·012	·109

Total increase: 1·002 grammes 5·57 grammes per cubic metre.
Loss at scrubbers, 16·30 per cent.

(*b*) Method of Absorption and the subsequent Distillation of the Absorbent.[1]—Creosote oil, oleic acid, and nitrobenzene are suggested as absorbents. Now to work successfully on this principle, similar treatment must be aimed at to that given to the gas on a practical scale, hence it is obvious that the most suitable of the three absorbents is the first. It is important, however, that the creosote oil should be specially prepared. Wash oil should be distilled and the fraction distilling between 240° and 270° C. taken. This is washed with acid and soda, to remove tar acids, pyridine bases, etc., and allowed to stand in ice in order to freeze out the naphthalene. Four absorption bottles should be used, each being of sufficient capacity to hold 200 c.c. of absorbent, and should be of a pattern offering a maximum surface of contact. 100 to 200 litres of gas are passed at about 10 litres per hour. The contents of the four bottles are afterwards drained into a large distilling flask and distilled, 50 c.c. of light oil (excluding the water) are collected and the distillation stopped. A 50 c.c. capacity flask is fitted with a miniature fractioning column and condenser, the latter being moistened with benzol and allowed to drain. 50 c.c. of a representative sample of the day's make of crude benzol (made on the plant the same day) are placed in the flask and distilled up to 160° C., correction being made for the barometric pressure; the yield is noted and the experiment is repeated, using the 50 c.c. of absorbent distillate.

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[1] By the Author (*Gas World*, Coking Section, May 1917).

Example.—100 litres of gas have passed through the absorbent which, on distillation and redistillation of the distillate up to 160° C. yields 3·0 c.c., and also 50 c.c. of crude benzol when distilled to 160° C. yield 37·5 c.c

Then, if 37·5 c.c. (100 per cent. at 160° C.) represent 50 c.c. crude benzol,
3·0 c.c. (100 per cent. at 160° C.) „ 4·0 c.c. „ „

Therefore there will be 4·00 c.c. of crude benzol, of the same strength as that made on the plant the same day in the absorbent, which represents 100 litres of gas.

Nitration Method.[1]—The same apparatus is required as for Muller's test. The first and second absorption bottles contain a mixture of nitric and sulphuric acids in the proportion of 70 per cent. sulphuric and 30 per cent. nitric.

No. 3 bottle contains distilled water, and
No. 4 „ „ 2 N/1 caustic soda solution.
The U tube contains calcium chloride.

Nitration of all the aromatics takes place in the first two bottles and nitrous vapours are caught in the last two, water vapour passing from the last bottle being caught by the U tube. The test is carried out as in the Muller's test, with the exception that ice is not required.

(*c*) **Vapour Pressure Method.**—The following method and description of apparatus was given by Burrell and Robertson of the U.S. Bureau of Mines 1915, and set forth by Mr Louis C. Whiton in a contribution to the *Journal of Industrial and Engineering Chemistry.*

The apparatus consists of a bulb 6 inches long, having a slight constriction in the centre. The upper portion of the bulb contains glass wool mixed with phosphorus pentoxide to extract all the moisture from the gas. Connected with this bulb is a mercury manometer and an entry and exit tube with a ground glass three-way cock. The air is first evacuated by means of a vacuum pump, the gas to be tested is sucked in, and the three-way cock turned when the gas is under barometric pressure. The entire bulb is then placed in liquid air in a Dewar's flask or in a mixture of CO_2-snow mixed to a consistency of slush with alcohol or acetone. It is allowed to remain there for ten minutes, the temperature being approximately −78° C. The benzol freezes out at this temperature, and the CO_2 O_2 CO . H_2 . CH_4 . N_2 . and C_2H_4, which have a high vapour pressure at this temperature, are evacuated by means of the vacuum pump, the cock turned to seal the system, and the apparatus brought to the room temperature. The partial pressure of the benzol vapour is registered on the manometer, and this result divided by the barometric pressure × 100 indicates the per cent. of benzol.

The above method has been slightly modified by Dr H. F. Coward, a

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[1] By the Author (*Gas World,* Coking Section. May 1917).

U tube having ground glass stoppers being used as the phosphorus pentoxide container. By this method Dr Coward claims to make an estimation of benzene and its homologues in a sample of coal gas in 15 minutes, obtaining figures corresponding with the yields of the plant.

(d) The Lessing "Dry" Process.—Dr Lessing, in a paper to the London Section of the Society of Chemical Industry,[1] describes the following apparatus, a diagrammatic view of which is given in fig. 10, and general view in fig. 11. The container A is filled with oil-soaked porous material C, which rests on a perforated bottom B, and exerts only a negligible back-pressure to the gas. The gas to be tested enters through the stop-cock D, passes downwards through the material and through the gas outlet E into the gas meter. The use of rubber tubing should be avoided as far as possible. The container A is surrounded by a jacket G, which is provided with a gauge H, and drain-cock J, and is filled with water during the scrubbing period. The gas is passed through the apparatus at the rate of about 5 cubic feet per hour, and about 100 cubic feet are used for one experiment. This will, therefore, cover a period of twenty hours during which time the

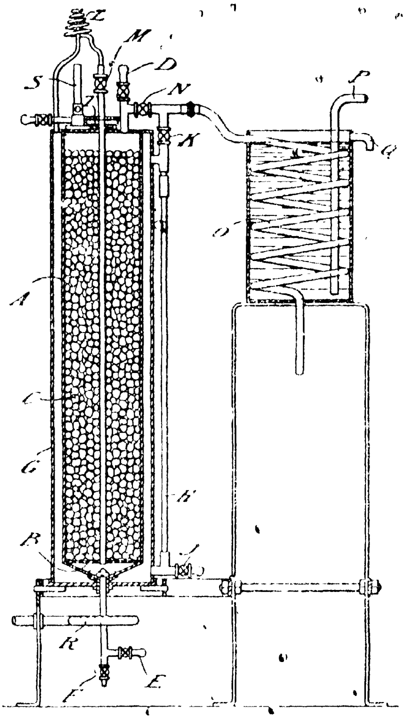

FIG. 10.

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[1] *Jour. Soc. Chem. Ind.*, February 1917, and *Gas World*, March 3rd

apparatus does not require any attention at all. Stop-cocks E and D are then closed, K is opened and the water run out through the drain-cock J, until it fills only about one-third of the jacket. A gas ring burner R is then lit and steam is raised in the jacket, the excess steam escaping through the condenser O. When the water is well boiling, K is shut and stop-cocks M and N are opened, the pressure having been relieved from time to time through N; at the same time the bunsen burner S is lit. The steam raised in the jacket now passes through the superheater coil L and stop-cock M to the bottom of the inner container and up through the absorbent material. The steam and vapour pass through N and condenser O. The products of distillation are collected in a graduated funnel clamped to the stand under O.

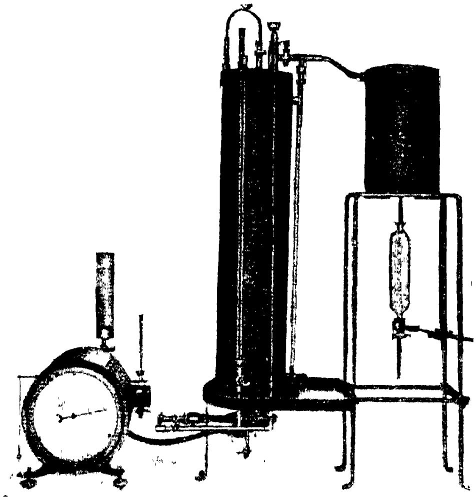

Fig. 11.

P is the inlet for the cooling water and Q its overflow. The charging hole T, through which the material is put into the apparatus, is closed by a screw-cap; any water condensing in the vessel or surplus oil is drawn off through drain-cock F. The steam distillation, including heating up, takes from one to one and a half hours, and is usually carried out until the absorbed naphthalene is distilled over. To avoid blockages in the condenser it is advisable to allow the cooling water to get hot before the naphthalene stage is reached. By drawing off the hot water and running cold water through the jacket the apparatus cools rapidly, and is then ready for scrubbing again, so that the complete cycle of operations can be carried out within twenty-four hours, and therefore daily tests can be made.

In the subsequent estimation of benzol and toluol Dr H. G. Colman's method is followed.

Freezing Method.—Quite recently a new method was suggested by Emile Sainte-Claire-Deville of Paris, and which the Author, having slightly modified it, strongly recommends where the apparatus is obtainable, the figures obtained being extremely accurate.

The principle upon which the method is based is, that if after drying the gas it is cooled to a very low temperature, the crude benzol becomes frozen and can be collected in a suitable vessel.

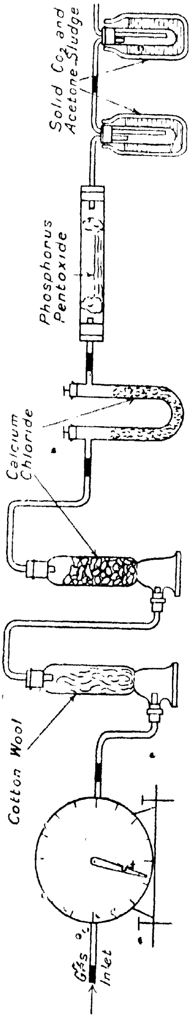

Fig. 12.

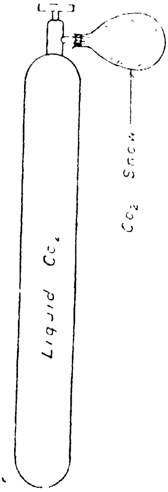

Fig. 13.

The apparatus used is shown (fig. 12).

Gas is passed through the meter, and then cleaned and dried by passing through cotton wool to remove suspended matter, and through two calcium chloride vessels to remove the bulk of the water vapour, the final traces of which being removed by a tube containing phosphorus pentoxide.

The clean dry gas then passes through two empty absorption tubes, surrounded by a mixture of acetone and carbon-dioxide-snow, mixed to the consistency of a thin paste, contained in two Dewar's flasks.

A temperature of − 72° C. is obtainable, at which all the constituents of crude benzol are solid.

By removing from the freezing mixture and allowing to rise to the temperature of the atmosphere, the solid mass melts, and can be either measured or weighed. Another point of advantage is that the resulting benzol is entirely free from traces of an absorbent, and therefore can be used for accurate analysis.

The carbon-dioxide-snow is prepared by tying a fine canvas bag over the outlet of a cylinder of liquid carbon dioxide and opening the valve (fig. 13), the reduction of temperature, owing to the sudden expansion, being sufficient to form solid carbon dioxide, which collects in the bag.

CHAPTER III.

ANALYSIS OF THE GAS.

Sampling.—Samples of gas are usually obtained by means of a sample tube (fig. 14). The bulb C and tube A are completely filled with water and connected up to the pipe from which the sample is to be taken as shown. First open tap D and then E, and allow the water to run out until the level G is reached; gas taking its place. Quickly turn off E and D and disconnect from A.

Hempel's Apparatus.—Measuring a definite volume of gas for analysis is performed in a Hempel gas burette shown A, B, C (fig. 15), and consists of two tubes A and B, which are joined by a long piece of thick-walled rubber tubing C. The tube B is the measuring tube and is calibrated from 0 to 100 c.c. in $\frac{1}{5}$ths of a c.c. from the bottom. The tube A is a levelling tube. The measuring tube is fitted with a glass tap, to which is fixed a piece of glass capillary tube S, bent as shown. Water is poured into the levelling tube until both tubes are about half full, care being taken to remove trapped air bubbles from the connecting tubing C. The levelling tube is then raised with the left hand, and the glass tap W opened with the right, until the water completely fills the measuring tube and begins to overflow, when the tap W is closed.

To transfer 100 c.c. of gas from the sample tube (fig. 14) to the measuring tube, the former is clamped in a vertical position, to the bottom tube being fastened a short length of glass tube dipping into a beaker of water, the top being connected to the glass capillary tube S. The levelling tube is then placed on the floor and the glass taps W, D, and E are opened in the above order Gas streams into the measuring tube, the displaced water passing into the levelling tube. The gas drawn from the sample tube is replaced by water drawn up the tube from the beaker. Rather more than 100 c.c. of gas should be allowed to enter the measuring tube, the three glass taps are then closed, and the levelling tube placed on the bench. The apparatus should be allowed to stand for about two minutes, to allow the water adhering to the walls of the burette to run to the bottom. The exact measuring of the 100 c c. of gas at atmospheric pressure is carried out by bringing the eye to the level of zero mark and compressing the rubber tubing C between the fingers until the liquid stands exactly at the same. To reduce the over-pressure in the levelling tube while the rubber tube is pressed tight, the tap W is opened for a moment, 100 c.c. of the gas then standing under the required conditions of temperature and pressure. This is confirmed by holding the two tubes by the iron feet so that the meniscus in both tubes are exactly level. The bottom of the meniscus in the measuring tube should stand exactly at 0.

The absorption pipette shown in fig. 15 is one of the series used with the apparatus and is known as the simple pipette. The portion D is filled with 25 per cent. caustic potash solution, which reaches into the syphon bend of the capillary tube up to the mark F, the bulb E remaining nearly empty.

In order to make an absorption, the capillary U tube is connected with the burette by the capillary tube S. The tap W and the pinch-cock V are opened, and on raising the levelling tube the gas is driven over into D, where it displaces liquid into E. When the whole of the gas has been transferred, the pinch-cock is closed and the burette disconnected, the absorption is expedited by well shaking the pipette. When absorption is complete, the burette is reconnected and the gas drawn back into the latter for measurement, taking care to bring the level of the caustic potash solution back to the mark F. The pinch-cock and tap are closed and the burette again disconnected. The gas is brought to atmospheric pressure, as

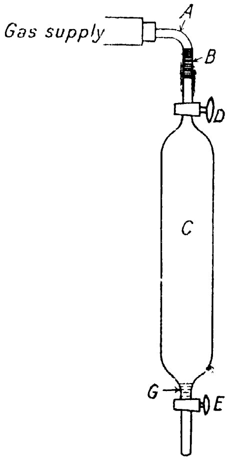

FIG. 14.

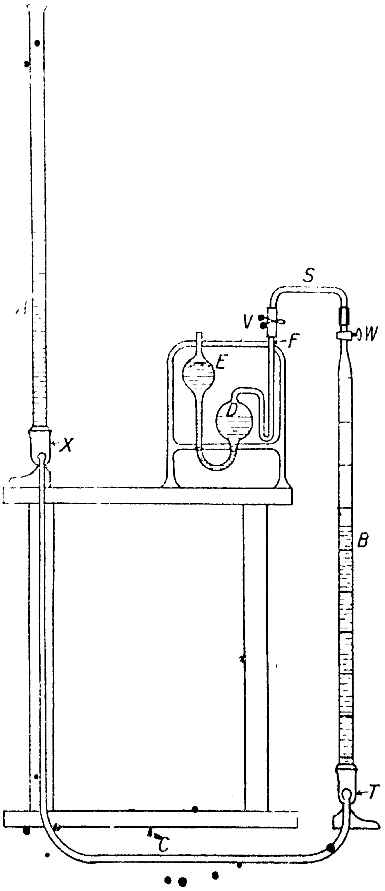

FIG. 15.

before, by bringing the meniscus in both tubes to the same level. The reading is noted, the figure representing the number of c.c. of the gas absorbed, or otherwise the percentage of carbon dioxide, caustic potash solution being an excellent absorbent for this gas.

The caustic potash pipette is then replaced by a double pipette (fig. 16).

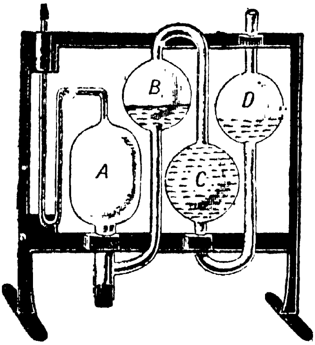

Fig 16

The bulbs A and B are filled with pyrogallate of potash solution prepared by dissolving 20 grammes of pyrogallol in 200 c.c. of a 25 per cent. solution of caustic potash, for the absorption of oxygen. The bulbs C and D are filled with water. The two bulbs A and B work exactly as the two in the "simple pipette." The last two bulbs C and D working with them and merely serving as a protection for the pyrogallate of potash solution from the oxygen of the air. The difference between the levels in the burette before and after the absorption being the percentage of oxygen.

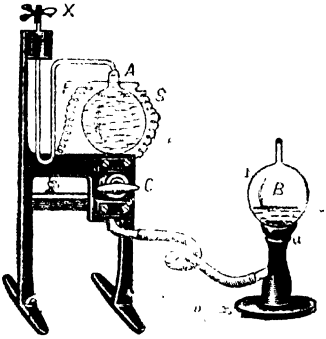

Fig. 17

The next pipette contains fuming sulphuric acid for the absorption of olefines and benzene vapour, this being followed by another double pipette containing acid cuprous chloride solution for the absorption of carbonic oxide, the solution being prepared by dissolving 30 grams of the solid in 50 c.c. of water and 150 c.c. strong hydrochloric acid, the solution being kept in contact with copper strips, in order to keep it reduced. There is then left for estimation, hydrogen, methane, and nitrogen. The burette containing the unabsorbed gases is connected to an aspirator bottle filled with oxygen, and by lowering the levelling tube, oxygen is drawn into the burette until the mixture of residual gases and oxygen again show 100 c.c., the tap being closed when the volume rises at atmospheric pressure to that mark.

The explosion pipette (fig. 17) is then attached, the two bulbs A and B being filled with mercury. The gases passed into A and the glass tap C and pinch-cock X are closed, the burette also being disconnected. An electric spark is caused to pass across the top of the bulb A by connecting the two wires P and S, fused through the walls of the bulb, to either a magneto or to an induction coil, driven by a dry battery. After the explosion open the tap C and reconnect on the burette, pass the residual gases into the latter and measure the contraction. Hydrogen combining with the oxygen forms water, and methane on burning produces its own volume of carbon dioxide. The amount of the latter produced is ascertained by passing the gases into the caustic potash pipette again and measuring the further contraction.

The contraction after the explosion, minus twice the volume of carbon dioxide found (representing the contraction due to the methane and its required oxygen), gives the contraction due to the hydrogen and its required amount of oxygen to form water vapour. Now, $\frac{2}{3}$ by volume of water vapour is hydrogen, therefore $\frac{2}{3}$ of this last portion of the contraction denotes the percentage of hydrogen. Nitrogen is obtained by subtraction

PRODUCER GAS.

Example—

			The total from 100 *per cent.*
After passing the caustic potash pipette	10·6 c.c.	absorbed	10·6% CO_2.
,, ,, pyrogallate of potash pipette	11·0	,, ,,	0·4% O_2.
,, ,, fuming sulphuric acid pipette	11·0	,, ,,	0·0% C_2H_4.
,, ,, cuprous chloride pipette	30·0	,, ,,	19·0% CO.
Residue left	70·0	,, ,,	
Made up to	100·0	,, with oxygen.	
After exploding, contraction	21·4	,,	
,, second absorption by caustic potash	22·2	,,	0·8% CH_4.
Now hydrogen $21{\cdot}4-(2\times{\cdot}8)=19{\cdot}8\times\frac{2}{3}$			12·2% H_2
Nitrogen by difference			57·0% N_2

COKE OVEN GAS.

Example—

After passing the caustic potash pipette	2·0 c.c.	absorbed	2·0% CO_2.
,, ,, pyrogallate of potash pipette	2·4	,, ,,	= 0·4% O_2.
,, ,, fuming sulphuric acid pipette	4·8	,, ,,	= 2·4% C_2H_4.
,, ,, cuprous chloride pipette	9·8	,, ,,	= 5·0% CO.
Residue left	90·2	,, ,,	
Half this volume of made up to	100·0	,, with oxygen.	
After exploding, contraction	68·7	,,	
,, second absorption by caustic potash	82·8	$= 14{\cdot}1\times 2$	$= 28{\cdot}2$% CH_4.
Now hydrogen $68{\cdot}7-(2\times 14{\cdot}1)=40{\cdot}5\times\frac{2}{3}\times 2$			= 54·0% H_2.
Nitrogen by difference			= 8·0% N_2.

Orsat-Lunge Apparatus.—This apparatus (fig. 18) is contained in a wooden box with removable back and front for convenience of transport, and consists of a measuring burette B, having a capacity of 100 c.c., contained in a water jacket, and connected at its base with a levelling bottle A, the top communicating by means of thick-walled, narrow-bore, glass tubing, provided with four branch tubes and stop-cocks, with four absorption pipettes, D, E, F, and G, filled with fine glass tubes placed vertically so as to present a large surface to the gas. The absorbent expelled by the pressure of the gas passes through a connecting tube into the rear portion of the pipette, which is similar in shape to the front portion, but empty, the top being connected to small bladders, in order to exclude air. The end of the capillary tube C communicating with the pipettes terminates in a three-way cock, by means of which the sample is drawn into the apparatus, or the contents can be placed under atmospheric conditions.

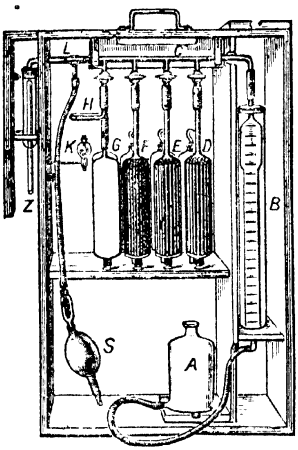

FIG. 18

The pipettes D, E, and F are filled respectively with solutions of caustic potash, pyrogallate of potash, and acid cuprous chloride, for the absorption of carbon dioxide, oxygen, and carbon monoxide; G is filled with water and connected to the glass capillary tube by means of a small bent tube H containing platinum or palladium asbestos, which is arranged so that it can be heated by the small spirit lamp K.

To carry out an analysis, place the water bottle A on the top of the case, and open the three-way cock D to the atmosphere, allowing the burette B to fill with water up to the capillary mark. Connect the end of the capillary tube Z with the gas supply, and the lower end of the three-way cock L with an india-rubber pump by means of which the air is removed from the conducting tube. The gas is now drawn into the burette by lowering the water levelling bottle and turning the three-way cock through 90 degrees, thus opening the apparatus to the gas supply at Z and cutting it off from the pump S. More than 100 c.c. of gas are drawn into the burette, the three-way cock is closed, and the gas compressed until the water level rises to the zero mark.

The connecting tubing is then squeezed by the fingers and the tap L is opened for an instant in order to put the burette under atmospheric pressure, when there will be exactly 100 c.c. of gas in the apparatus. The three gases CO_2, O_2, and CO are then absorbed in order by raising the levelling bottle and opening the tap on the corresponding pipette. The absorption is hastened by passing the gas from the burette to the pipette and back, several times, by alternately raising and lowering the levelling bottle. In each case, the absorption must be repeated until a constant reading is obtained on the burette, the readings of the latter being taken as with the Hempel apparatus.

The residual gas is halved by allowing a half of its volume to escape at L and the remainder made up to 100 c.c. with oxygen, all readings being made at atmospheric pressure. The spirit lamp is then lit, and when the tube H is hot, the mixture is forced through it into G, combustion taking place during its passage. Complete combustion is assured by passing the gas three times through H. The total contraction is measured, and the residual gas again passed into the caustic potash pipette D, the absorption representing methane. The percentage of hydrogen is calculated from the obtained data, in the same manner as with the Hempel apparatus; nitrogen being then obtained by difference.

Calorific Value.—(*Calculation from Analysis*).—When calorific values are required it is possible to calculate the same from the analysis, by multiplying the percentage of each combustible by the calorific value of that gas and dividing the result by 100, the results being added together.

Example—

Combustibles.	Analysis	B.Th Us per Cubic Foot				B.Th.Us.
Hydrogen	54·1	325	then	$\frac{54{\cdot}1 \cdot 325}{100}$	=	175·825
Methane	34·2	1024	,,	$\frac{34{\cdot}2 \times 1024}{100}$	=	350·208
Ethylene	3·0	1603	,,	$\frac{3{\cdot}0 \times 1603}{100}$	=	48·09
Benzene	1·0	3718	,,	$\frac{1 \times 3718}{100}$	=	37·18
Carbon monoxide	5·9	330	,,	$\frac{5{\cdot}9 \times 330}{100}$	=	19·47
Calorific value of gas in B.Th.Us. per cubic foot					=	630·773

For practical estimations of calorific values see "Calorimetry."

Specific Gravity of Gas.—The specific gravity of a sample of gas can also be calculated from the analysis in the same manner as the calorific value, substituting the specific gravity of the constituents. The following is a list of the various gases :—

Carbon dioxide	CO_2	1·529	Air = 1·000
Oxygen	O_2	1·105	
Carbon monoxide	CO	·955	
Methane	CH_4	·562	
Ethylene	C_2H_4	·982	
Hydrogen	H_2	·069	
Nitrogen	N_2	·971	

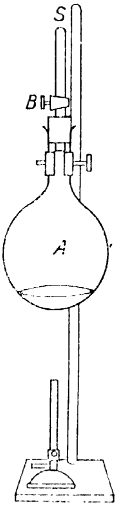

Fig. 19.

The results obtained should be checked by estimation in the following manner:—A 500 c.c. round-bottom flask A (fig. 19) is fitted with a rubber stopper, through which passes one limb of a glass stop-cock B. The flask and fittings are weighed dry, and then filled with water up to the stop-cock, and weighed again. The difference in weight gives the volume. The latter can also be estimated by filling with water and measuring it out again by means of a carefully graduated cylinder—the former method is, however, to be preferred.

Into the flask is then poured 15 c.c. of water, the stop-cock is opened and the water boiled until almost dry, the flask being then filled with steam. Whilst boiling, close the stop-cock and take away the bunsen burner simultaneously; wrap the flask in a duster and cool under a water tap, to the temperature of the room. Weigh the apparatus. Connect S with the gas supply, and cautiously open B, admitting gas to the flask. When filled, close B and reweigh. Pour out the water from the flask into a weighed beaker, allowing ample time for drainage, and reweigh. The difference in weight represents the volume in c.c. of the water in the flask. This deducted from the total volume of the flask gives the volume of gas admitted, the weight of which is found from the difference of the two weighings, before and after filling the flask with the gas.

$$\text{Specific gravity} = \frac{\text{Weight in grams.}}{\text{Volume in c.c.}}$$

CHAPTER IV.

FLUE GASES.

THESE are tested for carbon dioxide, oxygen, and carbon monoxide, usually in an Orsat-Lunge apparatus. The sample is obtained by passing into the chimney or flue an iron pipe about four feet in length and fitted with a rubber tube and pinch-cock, the hole round the pipe being made air-tight with cement or fireclay. The rubber tube is connected to a "Fletcher" aspirator, and the pinch-cock is opened. Gases are drawn through the pipe, sweeping out the air present, due to the draught of the chimney. The pinch-cock is then closed, and the aspirator replaced by the sample bottle fig. 14, or by the inlet to the Orsat apparatus. If the sample bottle is used, the lower limb must be sealed by means of a short length of rubber tube being attached which dips into a beaker filled with water, this preventing atmospheric air from being drawn into the sample bottle by the pull of the chimney. The test is then carried out in the same manner as with coal gas.

CO_2 Recorder.—There are quite a number of these instruments on the market, two of which are here described

The "Simmance Abady" CO_2 Recorder (fig. 20).—There are four vessels in this apparatus, which are termed respectively:—The Siphon Tank B, Extractor D, Recorder F, and KHO Vessel E.

A small stream of water is the motive power for effecting the whole of the operations described.

THE SIPHON TANK is furnished with a heavy float C, which rises slowly as the water fills up the tank, and falls quickly as the tank is emptied by the action of the siphon.

THE EXTRACTOR consists of a movable gas chamber D attached to the float by means of a chain M passing over two pulleys and working in an outer tank filled with water.

THE RECORDER consists of a small gas holder with internal standpipe and rising bell F suspended from a sensitive balance S moving over a divided scale N.

THE CAUSTIC POTASH (KHO) tank E consists of a steel tank fitted with gas inlet nipple and outlets, and furnished with an overflow pipe L closed with a pinch-cock for draining off excess.

A small WATER CISTERN K is fitted with a water connection and cock X with an injector nozzle A immediately below for exhausting the gases, and a loose valve J for discharging the contents of the cistern quickly at the moment of siphoning; a WASTE WATER TANK and outlet Y is also arranged in bottom of case to carry away the water after siphoning.

A non-return liquid seal U on the gas inlet P, with a safety-seal bubble bottle T on the injection connection P^1, are arranged on the side of the case.

Action of the Recorder.

Water is allowed to fall into the tank *B* from the cistern K. Assuming that the former is nearly full, and the weighted float C therefore near the top, then, as the water still continues to flow, the float will rise higher until it touches the end of the drip valve J, quickening the supply and starting the siphon, also actuating the pen (not shown on drawing). As the water siphons out, the float drops and pulls up the extractor D, and a charge of gas is drawn in from the flue-pipe through the non-return valve U. The siphoning being finished, and the water still continuing to flow, the float again rises and the extractor falls, gradually building up a pressure on the gas within, by the displacement of the surrounding water, sufficient to force

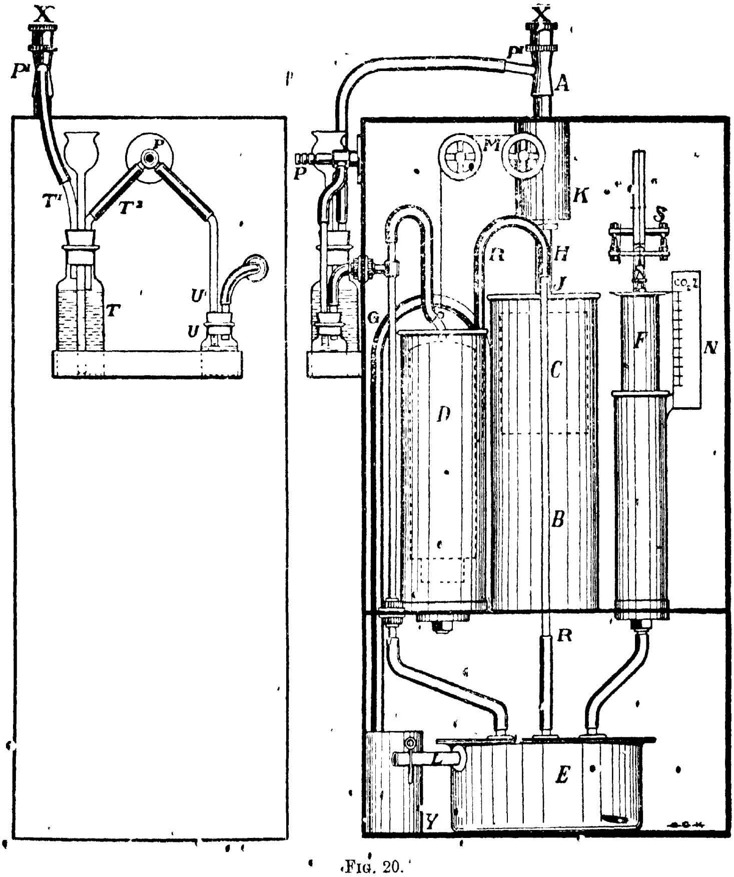

Fig. 20.

it through the KHO solution and out through vent pipe R until the end of the latter, which is fastened to the side of the extractor, is sealed in the water in the tank. On this point being reached, the remainder of the sample passes up into the recording bell as the extractor is lowered further into its tank.

The amount of gas trapped off in D by the sealing of the vent pipe, when transferred through the KHO, is just sufficient to raise the recording bell F from 100 to 0 when the apparatus is working on air containing practically no CO_2. When working on flue gas exactly the same quantity is passed from the extractor D, but on its passage the CO_2 is absorbed by the action of the KHO, and owing to such absorption the recorder bell F will not rise to its full height. It is allowed to automatically rise as far as it will and a pen then marks on the chart its final position, or the reading can be taken from the scale N. The percentage of CO_2 in the sample is thus automatically recorded. The pen is brought into operation by the last upward movement of the float, and the siphon again discharges and the whole operation is repeated, the bell F being vented and the analysed gas driven out through the vent pipe R as the latter is drawn out of the water.

It will be seen from the above that each sample is measured off under the same conditions of pressure, irrespective of the vacuum or pressure at which the bulk of the gas may be, this instrument being constructed to work accurately up to 3″ of vacuum.

(2) The "Albion" CO_2 Recorder.—Fig. 21 shows a diagrammatic section of the machine. A trickle of water runs into tank A until it overflows at the open end of pipe B, and falling into pan C, carried on lever D pivoted at E, fills, and depresses same, causing valve F to lift, allowing the water in A to run out quickly. Part of the water being directed by pipe G into pan, keeps it full until the water in A has fallen to level of valve box, when the siphon in pan C empties it, and the valve is closed by balance weight H. The filling action then recommences, and the cycle of operations is continued automatically. The water supply can be regulated to give a record every four to ten minutes as desired.

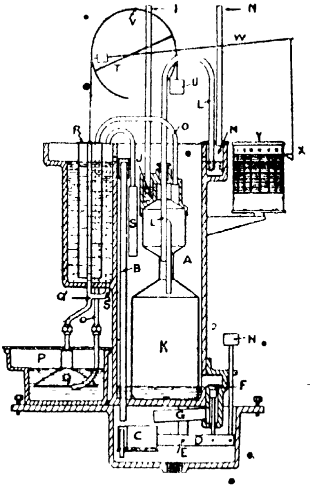

Fig. 21.

During the fall of water in tank A flue gas is drawn through pipe I, and its water seal J, and fills chamber K, and on the return of the water, part of this enclosed gas passes by pipe L through the water seal in box M, and escapes to the atmosphere through pipe N. When the water reaches the lower end of the pipe L, the remainder of the gas being entrapped is passed through the capillary tube O to the potash vessel P, bubbling through the solution which absorbs the CO_2, and the remainder collected under cone Q passes up the connecting pipe Q into bell R, causing it to lift. Since the pipe L is movable up or down, the quantity of gas retained in the upper part of K can be accurately adjusted, and when once set needs no correction.

The fall of the water in A uncovers that end of pipe S, which being a branch from Q allows the gas in R to escape, and the bell to fall to its normal position as shown.

The bell R is connected by a chain to the quadrant T balanced by weight U, and this revolves until 80 per cent. of the full stroke of bell is completed, when the stop V engages with the pen lever W and depresses same, and a line is drawn by pen X on the chart Y carried on a clockwork-driven drum.

It is obvious that the lift of the bell will vary according to the amount of CO_2 gas absorbed by the caustic potash, and the length of line drawn on chart will be longer when the proportion of CO_2 is smaller, and *vice versâ*. The bell is accurately balanced at all parts of its stroke by the varying radii of the quadrant, and the gas is under constant pressure.

The water level in bell tank, and the seals J and M are automatically maintained by ports communicating with the main tank A. Adjusting screws on the base plate permit of quick levelling of the machine, which is usually contained in a strong lock-up metal case with glass door.

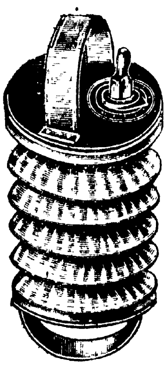

Fig. 22.

Sulphur Dioxide.—This is estimated by means of a "Fletcher" aspirator (fig. 22). 5·0 c.c. of hydrogen peroxide and 150 c.c. of distilled water are placed in the aspirator and half a cubic foot of gas is washed with it, by filling the aspirator, which holds $\frac{1}{10}$ cubic foot, five times, thoroughly shaking each time. The solution is then poured into a white basin, the aspirator rinsed out with distilled water and the washings also added. Methyl orange is added, and the whole is titrated with a standard solution of sodium carbonate. The test is based upon the reaction

$$H_2O_2 + SO_2 = H_2SO_4.$$

The amount of sulphuric acid being found by titration, and this being calculated to sulphur dioxide. With a normal solution of sodium carbonate, a certain amount of calculation is necessary for each estimation, therefore usually where a number of tests have to be carried out daily, a standard solution is prepared, 1 c.c. of which represents ½ grain of SO_2. Hence if ½ cubic foot of gas is washed, the number of c.c. neutralised will represent the number of grains of SO_2 per cubic foot of gas.

Another method depends upon the reaction of SO_2 with iodine solution—a measured quantity of the gases being passed through the standard solution of iodine. The standard solutions used for this estimation may be the N/10 solutions, in which case 1 c.c. of the iodine (and therefore indirectly 1 c.c. of the thiosulphate) is equivalent to 0·0032 gram of sulphur dioxide. It is more convenient, however, and simplifies the calculations, to employ solutions of such a strength that 1 c.c. shall equal 1 c.c. SO_2 measured at N.T.P., *i.e.* 0·002867 gram SO_2 instead of 0·0032 gram. Such solutions will contain 11·379 grams of iodine, and 22·22 grams of sodium thiosulphate per litre respectively, and they may be prepared either by weighing out these quantities, or by diluting the ordinary N/10 solutions; 100 c.c. of the N/10 solution (both the iodine and the thiosulphate) being diluted to 111·6 c.c.

In cases where the percentage of sulphur dioxide in the gas under examination is very small, it is better to employ solutions of one-tenth this strength, in which 1 c.c. is equivalent to 0·1 c.c. SO_2. One hundred cubic centimetres of the standard iodine solution are placed in a flask fitted with a cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork, as shown (fig. 23). The former of these tubes is connected to a piece of narrow metal pipe G, which is thrust into the flue through which the furnace gases are passing. The other tube is attached to the large bottle A, filled with water, which serves as an aspirator. The water is allowed to flow slowly out of the bottle by means of the screw clamp, and is received in a litre cylinder. The flask containing the iodine is shaken at frequent intervals during the process. When the cylinder is full to the litre mark, it is either changed or the clamp is closed for a moment while the cylinder is emptied and then reopened—a record being made of the number of litres thus drawn off. During the experiment the temperature of the water is taken (which will be the temperature of the gas); and the height of the barometer is noted. When 8 or 10 litres of gas have in this way been aspirated through the iodine solution, the process is stopped and 25 c.c. of the iodine are transferred to a beaker and titrated with the standard thiosulphate. As soon as the red-brown colour of the iodine solution changes to a straw colour, one or two drops of dilute starch solution are added, and the thiosulphate admitted drop by drop, until the blue colour is discharged. A duplicate titration is made in a second portion of the solution.

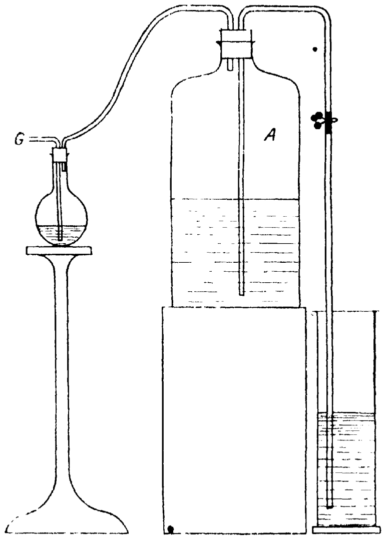

Fig. 23.

Example—

Gas drawn from the flue of a coke furnace.

Volume of water drawn from aspirator	8 litres.
Temperature	17° C.
Atmospheric pressure	760 mm.

Therefore volume of gas operated upon $= \frac{8 \times 273}{290} =$ 7·5307 litres at N.T.P.

100 c.c. of iodine employed in the absorption flask.

(1 c.c. = 1 c.c. thiosulphate = 0·1 c.c. SO_2 at N.T.P.)

After absorption, 25 c.c. iodine solution required 17 c.c. thiosulphate.

Volume of thiosulphate required for 100 c.c. = 17 4 = 68 c.c.

and volume of SO_2 absorbed $= \frac{100 \quad 68}{10} = 3{\cdot}2$ c.c.

Hence 7530·7 c.c. of the furnace gases contain 3·2 c.c. SO_2;

or $\frac{3{\cdot}2 \quad 100}{7530{\cdot}7} = 0{\cdot}425$ percentage SO_2 by volume.

CHAPTER V.

TAR DISTILLATION PLANT.

The Testing of Coal Tar.—*Specific Gravity.*—The specific gravity of samples of tars taken from various coke oven plants vary considerably, due to the different conditions under which the tar is extracted from the gas, and to the temperature of carbonisation. With thin tars, a fairly approximate result can be obtained by means of a Twaddle's hydrometer—the sample first being brought to 60° F.; but with thick tar other methods have to be used. The Author favours the use of the special specific gravity bottle, designed by Lunge and shown in fig. 24. The operation is performed as when estimating the specific gravity of solids thus:—

(1) Weight of bottle empty, ... $= a$
(2) " filled with water at 60° F., . $= b$
(3) " $\frac{2}{3}$ filled with tar, . . . $= c$
(4) " $\frac{2}{3}$ " , the remainder being filled up to the rill (a) with water, . . . $= d$

$$\text{The specific gravity} = \frac{C - A}{B + C - (A + D)}$$

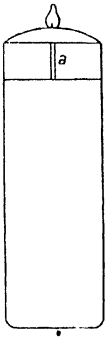

FIG. 24.

Tar containing water should first be dehydrated.

The specific gravity is a good guide as to the percentage of free carbon, the latter rising with the specific gravity.

Free Carbon.—(a) For rough comparisons of various tars the crucible test can be applied, as when testing coals—the free carbon being left behind after the volatile hydrocarbons have been driven off. This test can be very advantageously applied as a daily test of the quality of tar made, since any slight variation of quality will be immediately observed, and more thorough tests can be applied.

(b) An extraction thimble is placed into a Soxhlet's apparatus and extracted first with 90^s benzol, then with rectified xylene, and finally again with 90^s benzol, dried and weighed. Ten grams of the sample are then weighed into the thimble, the latter fixed again in the apparatus and extracted as before, extracting 40 to 50 times with each solvent and until it runs away colourless. The thimble is then removed from the Soxhlet tube, dried in a steam oven and weighed. Hooper recommends extraction 50 times each of:—(a) 90^s benzol, (b) rectified pyridine bases, and (c) unmineralised methylated spirit. Church's apparatus[1] is useful where a Soxhlet's apparatus is unobtainable.[2]

Moisture.—200 grams of tar are mixed with 25 c.c. benzol and 25 c.c. toluol, the whole being transferred to a distillation flask or retort, and very slowly distilled up to 200° C. The distillate, composed of water, benzol, and toluol, is collected in a graduated cylinder, and the amount of water read off. By carrying this test through slowly, the whole of the water is distilled over in less than 1 hour without frothing. Another method is to dry 100 grams of tar in a porcelain basin over a water bath until a constant weight is obtained, but this is only applicable to heavy tars such as those obtained from gas producers, etc., and which contain no low boiling substances, which would evaporate with the water, thus giving an erroneous figure.

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[1] *Coal Tar Distillation*, by A. R. Warnes, p. 229.

[2] See also Spielmann and Wood's method, *Free Carbon in Pitch*, p. 46.

Distillation Test.—The laboratory distillation tests of tar are at best only a rough guide as to the yields on a large scale, however, to a tar distiller they are invaluable, since they give a comparison of the value of the samples against that of a standard tar, the practical yields of which are known.

For laboratory testing 2240 grams are taken, each gram yield then representing a yield of 1 lb. per ton of tar.

Exactly 2240 grams of tar are weighed into a copper retort, fitted with a thermometer registering up to 400° C., and connected to a Liebig condenser, 24 inches long. The side of the retort is very gradually heated by means of a bunsen burner, no heat being applied to the bottom during the first hour, at the end of which time the flame is increased and allowed to play all round the upper part of the retort. When the thermometer registers about 80° C. the neck of the retort should be slowly heated, also the base of the retort should be heated at intervals, until the temperature rises to about 90° C., when oil and water will come over freely. At this stage the distillation must not be hurried, since, so long as there is water present, there is always the danger of the mixture frothing over; the test being thereby spoiled. At first far more water comes over than oil, but as the temperature rises more oil comes over and less water, until at about 185° C. no more water is seen in the distillate, the latter being a greenish yellow coloured oil. At this point the distillation is stopped. The distillate transferred to a separating funnel, and the water or ammoniacal liquor is run off into a tared 100 c.c. measuring cylinder and weighed, the volume at 60° F. being also noted. The specific gravity is calculated from these, and the ammonia content estimated by titration with N/1 sulphuric acid.

When the retort has been allowed to cool down, the separated oils from the distillate are returned to the retort, which is well shaken, and the distillation restarted, this time on dehydrated tar.

At first heat is slowly applied, but as the temperature rises it is increased. Distillation commences, with normal tar, at from 70° to 80° C., after which the temperature rapidly rises to 120° C., rising from this temperature more gradually.

The distillate up to 175° C. is collected in a tared measuring cylinder, at which temperature the cylinder is changed, being replaced by a larger one. The temperature is raised, the distillate coming over at a rate of one drop per second. The water-jacket of the Liebig condenser is emptied at this stage as a safeguard against the condenser blocking up with naphthalene. The receiver is again changed when a temperature of 220° C. is reached, and again at 275° C., the last fraction being collected up to 330° C.

We have thus—(1) ammoniacal liquor, (2) crude benzol up to 175° C., (3) carbolic oils from 175° C. to 220° C., (4) creosote oils from 220° C. to 275° C., (5) anthracene oil from 275° C. to 330° C., (6) pitch residue. Fractions Nos. 1, 2, and 3 are separately washed for crude tar acids and crude pyridine bases.

The tar acids are extracted by means of caustic soda, an aqueous solution of which should be at 20° Tw. (1·10 specific gravity). This solution is heated to about 50° C. The crude benzol fraction after weighing is put into a separating funnel, and washed with 10 per cent. of its own volume of the caustic soda solution for three minutes, by vigorously shaking the mixture, after which it is allowed to settle and the aqueous layer run into a flask. A second wash is proceeded with, using half the amount of caustic soda solution previously used, the latter also being added to the flask. The sodium phenate liquor is acidified with 40° T. (1·20 specific gravity) sulphuric acid solution, at the same time being kept cool under the water tap. Immediately the solution becomes acid the tar acids separate out in the form of a black oil which rises and forms a layer on the surface; they are allowed to settle, separated, and run into a tared measure. The tar acids are extracted from the carbolic oil in the same manner, but the first wash is carried out with double its volume of caustic soda solution, the second and third washes with half this amount. The acidifying is the same as with the crude benzol fraction, the yield of tar acids being added to the tared measure containing the yield from the crude benzol fraction. The total yield is weighed, the weight in grams representing the yield in lbs. per ton of tar.

Pyridine bases are extracted by washing with 50 per cent. sulphuric acid, 25 per cent. of the volume of the oils being tested being used three times. After allowing to settle, the acid layers are run off into a flask, made alkaline with 40° Tw. caustic soda solution, the mixture then being steamed, distilled, the distillate placed in a separating funnel, 90° Tw. caustic soda solution added until no more oil separates, the whole allowed to settle, the pyridine bases being weighed along with the washed benzol and light oil fractions.

The washed crude benzols and light oils are mixed together and transferred to a glass retort and distilled at a rate of 1 drop per second, separate receivers being used for the fractions. (1) up to 100° C., (2) 100° C. to 120° C., (3) 120° C. to 160° C., and (4) 160° C. to 190° C., the residue being added to the creosote oil fraction.

The creosote oil fraction usually contains a large amount of naphthalene. It is kept at a temperature of 60° F. for six hours. It is then filtered by means of a filter pump, until no more oil passes from it, the naphthalene on the filter paper being then pressed between other filter papers until free from oil (an old letter-press being excellent for this purpose), and weighed. The filtered oil, after washing out the tar acids and pyridine bases, is transferred to a tared measuring cylinder, weighed, and the volume noted, since the specific gravity of the various fractions is necessary to calculate weight into galls. per ton of tar.

The anthracene oil fraction contains a large amount of anthracene. It is therefore cooled to 60° F. for six hours, filtered, and pressed in the same way as in the creosote oil fraction. The anthracene cake thus obtained is dried at 100° C. for two hours, cooled and weighed. The volume and weight of the filtered oil is also taken.

The pitch is also weighed and calculated to one ton of tar.

The results of the analysis would be tabulated as follows:—

1. Ammoniacal liquor.
2. Benzol (up to 100° C.).
3. Toluol (100° C. to 120° C.).
4. Xylene (120° C. to 160° C.).

5. Naphtha (160° C. to 190° C.).
6. Crude tar acids.
7. Crude pyridine bases.
8. Washed creosote oil (190° C. to 270° C.).
9. Naphthalene.
10. Anthracene oil (270° C. to 330° C.).
11. Anthracene.
12. Pitch.

CHAPTER VI.

TESTING OF THE FRACTIONS OF TAR DISTILLATION.

(*a*) *Crude Benzol.*—For analysis of this fraction see crude 65^s benzol, page 81.

(*b*) *Crude Tar Acids.*—These are a mixture of phenol, ortha-, meta-, and para-cresols; ortha-, meta-, and para-xylols, and phenols of the anthracene series, together with small amounts of naphthalene and water.

These are usually tested, before further treatment, for the crystallisation point, and for the percentage of water, also for its specific gravity.

Specific Gravity.—This is determined usually by means of a hydrometer or a specific gravity bottle, the sample being first brought to 60° F.

Crystallisation Point and Water Content.—100 c.c. of the crude acids are placed in a retort and distilled slowly, the fractions being collected from the beak of the retort in dry measuring cylinders. All the water and 10 c.c. of the oil is collected in the first cylinder, the next 62·5 c.c. being collected in the second. The percentage of water is ascertained from the first cylinder; the second one is cooled slowly to near the expected crystallisation point, when a crystal of pure phenol is added, and the cooling continued, stirring continually with a Fahrenheit thermometer graduated in tenths of a degree. When the distillate is crystalline throughout, the temperature registered on the thermometer is taken as the crystallisation point.

Carbolic Acid in Crude Phenols.—Mm. René Masse and Henri Lerouse presented to the French Academy of Sciences, 9th Oct. 1916, a note upon[1] carbolic acid and the estimation of this in crude phenols from tar. The method still in use for the preparation of carbolic acid is that devised by Laurent in 1841, namely, (1) the separation of phenols from creosote oils by shaking up with soda; (2) the acidification to set free the crude phenols; and (3) the extraction of the carbolic acid by rectifications and crystallisations.

Good crude phenol, free from naphthalene, contains water, carbolic acid, ortha-cresol, meta-cresol, para-cresol, xylols, and homologues, and phenolic tarry matters. The chemical properties of carbolic acid and the cresols are so nearly related that there is no simple reagent which can separate them; thus Koppeschaar's bromine method will not work if both ortha-cresol and meta-cresol be present. The physical properties on the other hand do enable us to discriminate. The boiling points of phenol (carbolic acid), and ortha-cresol, meta-cresol, and para-cresol at 760 mm. barometric pressure are respectively 182°, 191·5°, 201·8°, and 201·2° C. Those of the xylols are 220° and 225° C. By fractionally distilling up to 203° C., then fractionally distilling up to 198° C., we can find the quantity of carbolic acid in each of these fractions by determining their respective crystallisation points. Commercial carbolic acid called 40° to 42° has a melting or solidifying point slightly above

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[1] *Gas World*, 9th Dec. 1916, p. 519.

40° C.; pure carbolic acid having 40·85° C. When we add cresols to pure carbolic acid, the melting point falls steadily, and that to very nearly the same extent whatever be the relative proportions of the three cresols, so long as the cresols added do not exceed 33 per cent. of the whole. The melting point of the mixture thus depends on the percentage of carbolic acid, and the curve of melting points is a straight line joining the two points (phenol 100 per cent., melting point 40·55° C.), and (66 per cent., melting point 21° C.). This is the basis of the following working method.

Three kilograms of crude acids are put in a four litre copper still with a Vigreux column of 24 inches. The distillation is maintained at 7 to 8 c.c. per minute, and the following fractions are taken:

(*a*) up to 180° C. (= water and phenols).
(*b*) 180° C. to 203° C.
(*c*) above 203° C., 100 c.c. only are taken.

To (*a*) add enough chloride of sodium (35 per cent.) to precipitate the phenols contained in it; decant these phenols and add them to (*b*). Put (*b*) into a flask of sufficient size; wash out the vessels with liquid (*c*), and add this to (*b*). The liquid (*b*) with its additions is now fractionally distilled at 4 c.c. per minute.

The fractions taken are from 250 to 300 grams each, until the temperature of the vapours reaches 198° C. The solidification point of each fraction is then determined. A test-tube determination gives a rough indication, but with 30 to 40 grams, allowed to cool slowly until supercooled by 1° or 2°, the addition of a trace of crystallised carbolic acid determines crystallisation, and the temperature goes up to the true melting point. If in the test-tube trial the required temperature is below 21° C. add carbolic in known quantity sufficient to bring the percentage of carbolic acid above 66.

This method enables the carbolic acid in a crude phenol to be estimated within one per cent., which is as near as could be expected with so complex a mixture as crude phenols.

Cresylic Acid, Separation of Isomeric Forms of Cresylic Acid.

The separation of the isomers, meta-, para-, and ortha-cresylic acids, can be carried out in the same manner as the practical process (German patents 137584 and 141421). According to this method the commercial cresol which contains meta- and para cresol after the separation of the ortha derivatives by freezing is heated with anhydrous oxalic acid, or an anhydrous acid oxalate. This produces para-cresol ester of oxalic acid which is removed from the solution by crystallisation, while the meta-cresol, which is not esterified, remains dissolved. The ester is a colourless solid substance, which is soluble in alcohol, ether, and glacial acetic acid, but insoluble in benzene. It can be purified by sublimation and decomposed by water.

The meta- and para-cresols can be separated also by obtaining the former in the form of a sulphonic acid, by treating the mixture with sodium bisulphate containing pyrosulphate at a temperature of 100° to 110° C., and separating the sulphonic acids obtained, or their sodium salts, from the unchanged para-cresol.

Water.—100 c.c. of the sample are carefully distilled in an 8-oz. retort until all the water and part of the oil have distilled over, being collected in a graduated cylinder; petroleum ether is added and the whole thoroughly shaken and allowed to stand, when a clear reading may be obtained.

Distillation Test.—100 c.c. of the sample are distilled from a distillation flask to which is connected an air-cooled condenser, the distillate being measured for every °C. rise from 194° C. to 204° C.

Neutral Oils.—100 grams of the sample are well shaken with a 20 per cent. solution of caustic soda, and allowed to stand. If all the oil has dissolved without turbidity, no neutral oils are present; but if a turbidity is perceived, the whole should be extracted with petroleum ether, the latter, after standing, being separated from the sodium cresylate solution, the petroleum ether slowly evaporated in a tared beaker, and the neutral oils left, and weighed.

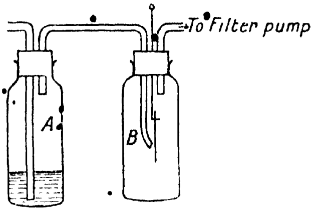

Fig. 25.

Sulphuretted Hydrogen.—50 c.c. of the sample are placed in the flask A (fig. 25), fitted with inlet and outlet tubes, the inlet tube dipping into the cresol and the outer tube connected to another flask B, which in its turn is connected to a filter pump. A piece of lead acetate paper hangs in B over the air inlet tube. The pump is started, and air is drawn through the cresol into the second bottle B, where it comes into contact with the lead acetate paper The time is noted for the paper to blacken. Good cresols will not blacken the paper until after 15 minutes.

PYRIDINE BASES.

Water.—The percentage of water is determined by means of a carbon colour-test tube (fig. 26), graduated into $\frac{1}{10}$ths of a c.c. This piece of apparatus can easily be made from a broken burette by cutting off a suitable length and sealing the end in a blow-pipe flame. Into the tube 23 c.c. of 80° Tw. caustic soda solution (which must be perfectly clear) are carefully run, and, if necessary, adjusted, after standing a short time.

To this, 25 c.c. of the sample are added, a cork inserted into the neck, and the contents gently shaken, after which they are allowed to stand for a short time to separate, the increase in volume of the caustic soda solution indicating the amount of water present.

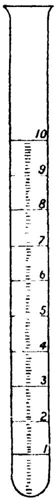

Fig. 26.

Distillation.—250 c.c. of the sample are dried by washing with 80° Tw. caustic soda solution, and distilled from a round-bottomed flask fitted with a fractionating head of the Bel Henninger type, the following fractions being measured and reported:

(1) All up to 140° C. (refined pyridine).
(2) 140° C. to 160° C. (refined heavy pyridine).
(3) 160° C. to 180° C. (heavy pyridine bases).

Creosote Oil.—*Specific Gravity.*—This is usually determined by means of a hydrometer at the temperature at which the oil is fully fluid; a correction being made for the temperature. Lunge gives us the following table from which we can calculate the true specific gravity of the oil at 60° F.

TABLE FOR REDUCING THE SPECIFIC GRAVITY OF OILS.

(1.) For specific gravities of ·800 and downwards.

Degrees C	2	4	6	8	10	12	13½	14½
Deduct	·0105	·009	008	·006	0045	·003	·002	0

Degrees C.	17½	19½	21½	23	25	27	29
Add	·001	0025	·004	·0055	007	·008	·010

(2.) For specific gravities between 880 and ·920.

Degrees C.	2	4	5½	7	9	10½	12	14
Deduct	01	·0085	·0075	0065	·005	004	·0025	·001

Degrees C.	15½	17	19	20½	22	24	25½	27	29
Add	0	·001	·0025	·0035	·005	·006	·007	·008	:0095

(3.) For specific gravities between ·920 and ·960.

Degrees C	1½	3	4½	6	7	8½	10	11½	13	14	15½
Deduct	·01	·009	·008	·007	·006	·005	·004	·003	·002	·001	0
Degrees C.	17	18	19½	21	22½	24	25	26½	28	29½	
Add	·001	·002	·003	·004	·005	·006	·007	·008	·009	·010	

(4.) For specific gravities above ·960, add ·001 for every degree above 15° C.

Water.—This is determined by distilling 100 c.c. of the oil from a retort until no more water is given off, and adding to the distillate, consisting of oil and water, about 10 c.c. benzol, which will result in a clear reading being obtained.

Distilling Range.—100 c.c. of the sample are placed in a 6 oz. retort, provided with a thermometer, the bulb of which is fixed ⅛ of an inch from the bottom. In place of a condenser a length of glass tube 2 feet long and 1 inch wide is used. The retort is heated by a small flame and the drop point is noted, *i.e.* the temperature at which the first drop runs into the graduated cylinder used as a receiver. The distillation is carried on at the rate of two drops per second, and the amount distilled over is measured every 10° C. rise from 200° to 300 °C. when the burner is removed.

If much water is present, the distillation should be stopped at 200° C., any oil distilled over separated from the water and returned to the flask, when the latter has cooled, the distillation then being recommenced.

Phenols.—The distillate is washed three to four times with warm 20° Tw. caustic soda solution, running the phenolate solutions into a separating funnel and acidifying with 40° Tw. sulphuric acid. The whole is allowed to stand for an hour, and the layer of crude phenols measured.

Naphthalene.—The washed oil is then allowed to stand for 24 hours at 60° F., filtered by means of a filter pump, the precipitated naphthalene pressed between filter papers until free from oil, and weighed. According to a pamphlet circulated December 1917, the Controller of Munitions Mineral Oil Production recommends the method described by J. C. Mann, which is analogous to the method commonly employed for ascertaining the crystallising point of commercial carbolic acid. The apparatus (fig. 27) consists of a test-tube about 4 to 5 inches long, and ⅝-inch diameter, fitted concentrically, by means of a bored cork in a wider test-tube about 7 inches long by 1½ inches diameter, the space between the two tubes forming an air-jacket. The combined tubes are placed vertically in a vessel of suitable size, filled with water. The inner test-tube is fitted with an accurate thermometer capable of being read to ·2° C. or ·5° F. fixed concentrically within the tube by means of a bored cork, the bulb of the thermometer being fixed at a height which allows of the temperatures 5° to 20° C. or 40° to 70° F. being conveniently read off. The tube is also provided with a stirrer made of copper wire, a nick being cut in the side of cork carrying the thermometer to allow of this stirrer being moved up and down. In carrying out the test, an average sample of the creosote previously freed from traces of water by shaking with ignited calcium chloride, is first cooled quickly, stirring with the thermometer, and an approximate idea of the crystallising point gained by noting the temperature at which naphthalene separation is manifest. The inner tube of the apparatus is then filled with the dried sample of the creosote to about two-thirds of its capacity, and so that the thermometer bulb is not less than 2 c.c. below the surface of the creosote and the latter also well below the under side of the cork of the air-jacket. The creosote before adding must be at a temperature at which it is completely liquid.

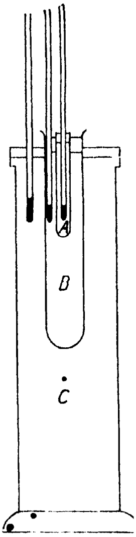

FIG. 27.

Water is then placed in the water-jacket at a temperature of 2° to 3° C., lower than the approximate crystallising point above observed, and the double tube containing the creosote immersed completely in the water to the level of the cork.

The thermometer in the creosote is then observed without stirring until the fall of temperature ceases. The creosote is then vigorously stirred with the wire, when the temperature rises and the rise continues until a maximum is reached which is noted.

The maximum point attained is taken as the crystallising point.

From a curve plotted from the following data the percentage of naphthalene in any sample may be found.

Percentage of Naphthalene.	Crystallising Point.	Percentage of Naphthalene.	Crystallising Point.
20	30° C.	35	45·5° C.
25	34° C.	40	49·8° C.
30	40° C.	45	52° C.

Pyridine Bases.—100 c.c. of the sample are distilled up to 300° C., the distillate washed three times with 40 per cent. sulphuric acid, the acid extractions collected together, and the pyridine bases thrown out by the addition of 40° Tw. caustic soda solution. These are dried by shaking up with 90° Tw. soda solution, and measured.

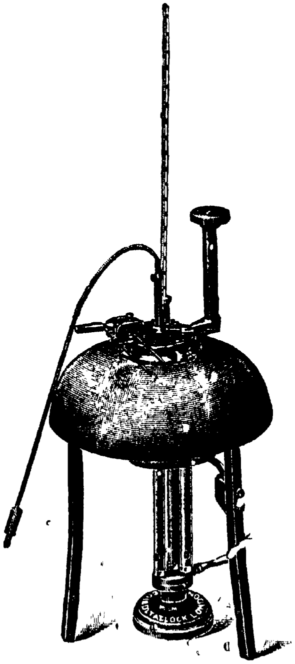

FIG. 28.

Flash Point.—The Abel apparatus is not suitable for testing the flash point of creosote, the latter being too high. There are, however, other forms of apparatus—namely, (1) the Pensky-Marten, and (2) the Gray—which are designed for use with heavy oils.

(*a*) *The Pensky-Marten Tester* (fig. 28). The cup is of the same dimensions as that of the Abel apparatus, and the lid has an arrangement for the application of the test flame in a similar manner to the one adopted with that instrument, but a modification enables the test to be applied by turning a non-conducting button. Before determining the closed test, the cup and lid, with the attached stirrers, are very thoroughly cleaned from any oil remaining from a previous sample. By forcing the manipulating button upwards, the revolving plate on the cover may be removed, and the cleaning facilitated. If the oil last under examination was of a much more volatile nature than the sample in question it may be well to reject the result of the first test, using the first test as a means of freeing the cup from any foreign vapour. When thoroughly cleansed the cup must be filled to the line inscribed, the lid put on so that it is well 'home' and the cup placed in the air-bath. The heating by means of a bunsen burner under the air-bath for at least 50° below the flash point is to be at the rate of 10° a minute, and the test is to be applied at every 2° F. rise. During the whole experiment, the stirrers must be kept revolving with a steady continuous motion, but during the actual application of the test-flame it is usual to cease agitation. Care should be taken that in stirring none of the oil is thrown up on to the lid of the cup.

(*b*) *The Gray Tester* (fig. 29). The chief variation from the Pensky Marten consists in the means for rotating the stirrer and for applying the test-flame. Both these operations are performed from a non-conducting button fixed on the end of a horizontal shaft which also carries one of a pair of bevelled wheels, and is pierced by a short pin. The other bevelled wheel is fixed on the upper end of the spindle to which the stirrer is attached. Thus by turning the button slowly by means of its handle the oil is kept gently agitated. In making a test the horizontal shaft is slid back (a certain amount of "play" being allowed it by the supports) until the pin engages with a projection attached to the sliding cover of the lid, then, by grasping the button itself and turning it firmly the cover is opened.

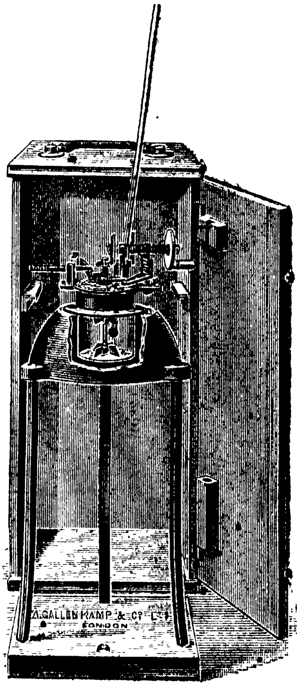

FIG. 29.

The results furnished by the Gray should be concordant with those obtained by the Pensky Marten.

Viscosity.—The "body" or viscosity of the oil is most commonly measured by its rate of flow through an orifice of certain dimensions. The results obtained are compared with those obtained from a standard sample.

Redwood Viscometer.—(figs. 30 and 31).[1] This instrument consists of a silvered brass oil cylinder, furnished with an agate jet, and surrounded by a copper bath. A copper tube, closed at the lower end, projecting at an angle of 45 degrees from the side of the bath near the bottom, provides a means of heating the bath liquid, and by the use of a revolving agitator, which forms part of the apparatus, the heated liquid rising from the copper tube can be uniformly distributed through the bath. The agitator carries a thermometer to indicate the temperature of the bath. The oil cylinder is furnished with a stopper, consisting of a small brass sphere attached to a wire, the sphere resting in a hemispherical cavity in the agate jet. A short standard attached to the oil cylinder carries a clip to support a thermometer in the oil. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket, terminating in an upturned point, which forms a gauge of the height of the oil level. The instrument is supported on a tripod stand provided with levelling screws.

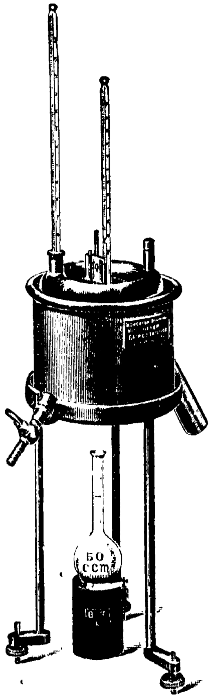

Fig. 30.

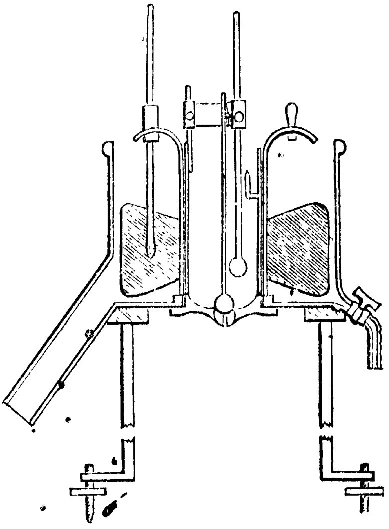

Fig. 31.

Directions for Use.

The bath is filled with a suitable liquid to a height roughly corresponding with the point of the gauge in the oil cylinder. Water answers well for temperatures up to 200° F., and for higher temperatures a heavy mineral oil may be used. The liquid having been brought to the required temperature, the oil to be tested, previously brought to the same temperature, is poured into the oil cylinder until the level of the liquid just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop-watch at the same time started, and the number of the seconds occupied in the outflow of 50 c.c. noted. It is of the greatest importance that the oil cylinder should be filled exactly to the point of the gauge after inserting the thermometer, and that the given temperature should be precisely maintained during the experiment, a difference of $\frac{1}{2}$° F. making an appreciable alteration in the viscosity of some oils. It is also essential that the oil should be quite free from dirt or other suspended matter, and from globules of water, as the jet may be otherwise partially obstructed. If the oil-cylinder requires to be wiped out, paper rather than cloth should be employed, as filaments of the latter may be left adhering. When oils are being tested at temperatures much above that of the laboratory a gas flame is applied to the copper tube and the agitator kept in gentle motion throughout the experiment.

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[1] *Journ. Soc. Chem. Ind.*, March 1886; *Petroleum*, p. 600.

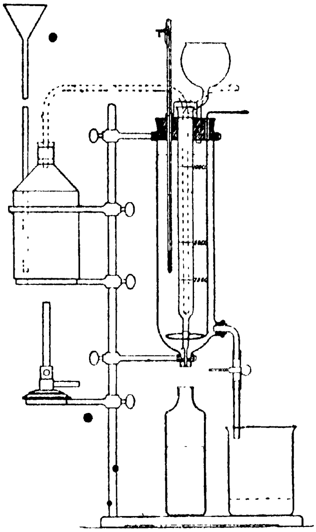

Fig. 32.

Note.—The jet should be carefully examined before the apparatus is used, and, if necessary, should be cleaned by passing a piece of soft string through it. The apparatus should be adjusted by means of the levelling screws, so that a spirit-level placed on the top of the oil cup shows it to be horizontal.

Sir Boverton Redwood recommends that the number of seconds occupied in the outflow of 50 c.c. of the oil under examination should be multiplied by

100 and divided by 535 (the number of seconds occupied in the outflow of 50 c.c. of average refined rape oil at 60° F.). The resulting figure should then be multiplied by the specific gravity of the sample at the temperature of the experiment and divided by 915 (the specific gravity of the refined rape oil at 60° F.). The final figures will express the viscosity of the oil at the temperature of the test in terms of viscosity of refined rape oil at 60° F.

Coleman-Archbutt Viscometer (fig. 32).—This instrument is an improved form of the well-known jacketed glass viscometer, first used by Coleman about 1869. It consists of a glass burette contained in an outer jacket, with a funnel for pouring in hot or cold water, a tube for running off water, and a stirrer for thoroughly mixing the water in the jacket. Being made of glass it is fragile, but with reasonable care an instrument may last for many years. It may be standardized with glycerine so as to give results in absolute measure, and it has the advantage of being very convenient to work with. Thus, the temperature of the oil can be readily adjusted in the efflux tube itself by stirring with a thermometer and raising or lowering the temperature of the water in the outer jacket. There is no need for a separate measuring vessel, the volume of oil which flows out being measured by marks on the efflux tube.

A test can be made with as little as 25 c.c. of oil, and after the test has been made the tube is empty and ready for the next test. Oils can be tested in this apparatus at the temperature of boiling water, which is high enough for most purposes.

Method of Experiment.—The tube A and jet are first carefully cleaned and dried. The jet is then closed by means of a small peg of soft wood. Water at the proper temperature is next poured into the jacket, and the oil, previously strained, if necessary, and brought to the same temperature, is poured into the efflux tube up to about half an inch above the mark it is intended to run it from. The oil is stirred with the thermometer, avoiding the formation of air bubbles, until the temperature is exactly correct, the final adjustment being easily made by slightly raising or lowering the temperature of the water-bath. The thermometer is then taken out of the oil, which is allowed to rest until perfectly quiescent. The wood peg is then withdrawn and the time taken by the oil to flow down to the zero mark is measured by a stop-watch, which is started as the surface of the oil passes the upper mark. During the experiment the temperature is maintained constant by pouring hot or cold water into the jacket through the funnel and running off the excess through the side tube as often as required, using the stirrer frequently. The temperature of the water in the outer jacket is indicated by the thermometer T, which is not removed. The open end of the efflux tube is covered by the inverted beaker K to prevent water from being splashed in by the stirrer.

In making an experiment at 212° F., the cold water in the jacket is first raised gradually to about 180° F. by pouring in hot water, and then the funnel is replaced by the steam tube L, and steam is blown in from the boiler. When the water boils the level is lowered sufficiently to prevent splashing, and a brisk ebullition is kept up throughout the test. The oil, previously heated to 212° F., should be poured in just before the water begins to boil and the tube A covered by its cap.

Relative Rates of Cooling.[1]—According to T. F. E. Rhead, the relative rates of cooling of creosotes are determined as follows:—10 c.c. of creosote are placed in A (fig. 33), a 50 c.c. Jena bulb, with the thermometer immersed in the centre of the liquid always to the same extent. Water at a constant temperature is circulated through the water-bath at a constant rate sufficient to prevent the temperature on the outside of A rising more than 1° C. as indicated by the thermometer in the water. A is heated to a uniform temperature of 120° C., then plunged into the water-bath (always in the same position in the bath), and the rate of fall of temperature is recorded in seconds, using a stop-watch. The experiment is stopped when the temperature reaches 15° C.

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[1] *Gas World*, 27th January 1917.

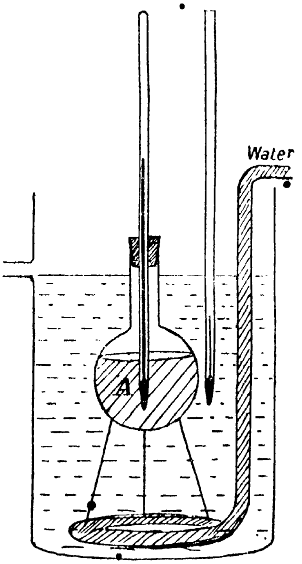

FIG. 33.

NAPHTHALENE.

Moisture.—Weigh out 200 grams, place in a distilling flask, add 50 c.c. toluol or xylol, and distil slowly until all the water has come over, which is then easily measured.

Foreign Matter.—Weigh out 200 grams of the sample, dissolve in 500 c.c. warm 90^s benzol, filter through a tared filter paper, wash the latter with 90^s benzol, dry and reweigh, the increase in weight being the foreign matter.

Melting Point.—A good works method is to fill a small saucepan with the sample, and warm until the contents are completely melted. A finely graduated thermometer is then fixed with the bulb in the centre of the naphthalene, and the whole allowed to cool.

The temperature recorded on the thermometer will be seen to fall steadily until crystals appear on the surface of the liquid, when it will rise about two degrees, remaining constant then for a considerable time. This is taken as the melting point or crystallising point. For more delicate work Kleinhardt's melting point apparatus is used (fig 34). Melt some of the substance to be tested and fill one of the tubes B up to the mark K. While still warm immerse the thermometer to the bottom of the tube, place same in the metal frame and immerse the whole into cold water or freezing mixture. After the substance solidifies, the tube and thermometer is supported as shown in the illustration ; vessel A is now filled with warm water about 5° to 10° C. above the assumed melting point of the substance. Carefully watch for the uncovering of mark D on the thermometer, which will be seen as soon as the tube B begins to drop, remove the whole and stir the substance with the thermometer until the temperature ceases to rise. The highest registered will accurately indicate the melting point, and, with a little practice, determinations can be made of $\frac{1}{2}$° C. Two or three tests can be made in one minute. The determination of quality lies in the fact that a high melting point indicates that the sample tested adhered to the thermometer longer than a sample with a lower melting point.

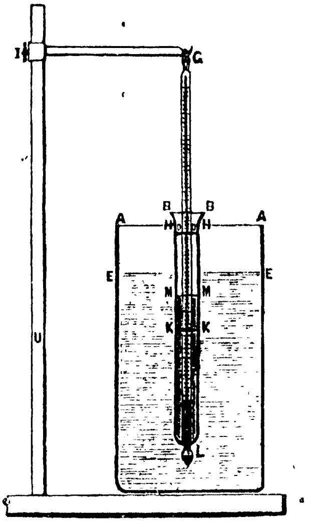

FIG. 34.

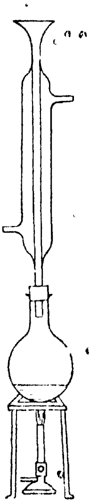

FIG. 35.

ANTHRACENE CAKE.

Moisture and Foreign Matter are tested for as with naphthalene.

Anthracene. — Hochst test. 1 gram of the sample is dissolved in 45 c.c. of glacial acetic acid, in a half-litre flask, to the mouth of which is connected an inverted condenser (fig. 35), and to this is added from a tap funnel, fitted to the top of the condenser, a solution of 15 grams of chromic acid in 10 c.c. of glacial acetic acid, diluted with its own volume of water. The contents of the flask must be kept in gentle ebullition and the chromic acid must be added, drop by drop, the operation taking about two hours. The liquid in the flask must then be kept boiling for two hours longer, when the heat is removed and the flask and contents left at rest for twelve hours. 400 c.c. of water are now added, and after leaving for three hours the contents of the flask are filtered, the anthraquinone collected on the filter is washed, in turn with cold water, boiling dilute solution of caustic potash (about 2 per cent.) and then with hot water.

The anthraquinone is transferred by washing from the filter to a porcelain dish and then dried at 100° C. Ten times its weight of fuming sulphuric acid are then added. The dish is heated on a water-bath for ten minutes and then placed in a moist atmosphere for 24 hours. 200 c.c. of water are added, the whole filtered, and the mass washed on the filter as before. The contents of the filter are transferred to a dish which is dried at 100° C. and weighed. The dish is then heated to drive off the anthraquinone, cooled and reweighed; the difference between the two weighings gives the amount of anthraquinone which, multiplied by ·8558, gives the weight of anthracene in 1 gram of crude cake.

Paraffin.—10 grams of the sample are weighed into a large beaker, 108 c.c. of concentrated sulphuric acid are added, and the mixture heated on a water-bath until all the anthracene is dissolved, when it is cooled and poured into 400 c.c. of cold water contained in a litre separating funnel. The mixture is allowed to cool and then extracted twice with light petroleum-ether (dry at 75° C.). The petroleum-ether extracts are bulked and washed in a separating funnel, first with half its bulk of 5° Tw. caustic soda solution, and then four times, with one-eighth of its bulk of cold concentrated sulphuric acid, and after this with cold water until free from acid. It is then allowed to settle, any water which separates removed, and then transferred to a tared flask, the ether distilled off and the residue weighed.

PITCH.

Twisting Point.—A sample of the pitch is slowly melted, care being taken that no volatile matter is driven off, the melted pitch being run into a mould ½ inch by ½ inch by 3 inches, and cooled. The cooled piece is suspended by a piece of string in a beaker of water, and the temperature of the latter is very slowly raised until 95° F. is reached, when the sample is taken out of the water and an endeavour made to twist it by means of the thumb and first finger on each hand.

It is very probable at this temperature that it will not twist easily. Therefore the pitch is immediately put back into the water, and is again tried at each degree rise in temperature until it twists without pressure. The temperature at which it twists is then recorded as the twisting point.

Volatile hydrocarbons and ash are tested for in the same manner as with coals.

THE ESTIMATION OF "FREE CARBON" IN TAR AND PITCH.

By Percy E. Spielmann, Ph.D., B.Sc., F.I.C., and Henry Wood.

It is universally accepted that "free carbon" in tar and pitch does not consist of carbon in the chemist's sense of the word, but of substances containing a high percentage of carbon, and having a very high molecular weight. These compounds show a very low solubility, so that accompanying substances can be extracted from them.

Personal experience has confirmed recently published work that the usual solvents employed did not all lead to the same results, so that serious discrepancies occurred between two different workers of equal trustworthiness.

The object of this investigation was to determine the extent and rate of extraction of the soluble substances in tar and pitch by various solvents; and also to ascertain the relative value of the several recommended methods and liquids. Incidentally some knowledge has been obtained as to the effect of the kind of still (when distilling tar) on the "free carbon" content of the resulting pitch.

The solvents used alone or in succession were benzole, carbon disulphide, carbon tetrachloride, ether, chloroform, xylole, pyridine, and a neutral tar oil. These were used in a Soxhlet extractor of the ordinary kind, and some determinations were made in a special form of Soxhlet hot extractor. In addition, a method used in works was also examined, namely, treating the sample with hot solvent and then filtering through an ordinary filter paper or a Gooch crucible, and subsequently washing with solvent. A hot vapour extraction was also tried.

It was found (Table B.) that benzene followed by CS_2 gave the lowest and most consistent result. Ether was so far successful that it removed nearly all the soluble material, but the final extraction was very slow. Carbon tetrachloride did not remove more than ether for about the same time of extraction, but was curious in that if followed by CS_2 and benzene the final figure for "carbon" was considerably higher than if the last two solvents were used alone. This would seem to confirm earlier observations as to changes brought about by carbon tetrachloride when used for the present purpose.

Neutral oils gave much trouble, and the extraction was very slow. Traces of moisture caused violent bumping and fracture of the flask. No consistent results could be obtained. Chloroform was not found to present any advantages over benzene and CS_2. Xylole was efficient, but slow. Pyridine extracted well, but corroded the corks so much that it was not convenient.

It was found that Soxhlet filter thimbles varied very greatly in quality, even among the products obtained from the same firms. Some acted satisfactorily, whilst in others definite cracks even were visible. After prolonged action of benzene and CS_2 it was noticed that the material of the thimbles was altered to such an extent that they could be rubbed to powder with the finger. As much trouble was experienced in retaining finely divided carbon even when the thimbles were of double thickness, the expedient was tried of placing one of ordinary thickness of smaller size within the thick one; this was, however, by no means always successful, and in the end two thin thimbles were found most satisfactory.

It was noticed that a considerable amount of solid matter had separated from the solvent in the flask by the time the extraction had come to an end; this, on filtration and repeated washing with solvents, remained undissolved to a great extent, thus confirming qualitatively the work of Monroe and Broderson.[1]

In order to obtain comparable results as far as possible, pitch was used; which, after being powdered, passed through a 60- but not through a 90-mesh sieve. Some experiments were made with the finest fractions of sieved material, but only very slightly different figures were obtained, and undoubtedly greater liability to caking in the thimble occurred.

With respect to the subsidiary part of the investigation, it was found that the commercial pitch contained less free carbon than a sample of pitch of the same softening point obtained in the laboratory from a copper flask; and further, that a pitch produced in a Colman's iron still (which was primarily designed to produce light fractions) contained a higher percentage of carbon than did a pitch of similar softening point obtained from the same tar distilled from a copper flask.

Method of Extraction.—Carefully dried solvents were used. 2 grams of 60-mesh powdered pitch were mixed with twice its bulk of washed sand. This was poured into the thimble and covered with a further small quantity of sand. Before beginning extraction, some solvent was placed in the extractor and the thimble and contents allowed to soak in it, a procedure which was found to assist in the prevention of material passing through walls of thimble.

A first series of extractions were made to determine the rate of extraction. The Soxhlet took 10 to 12 minutes in filling and emptying.

TABLE A.

Rate of extraction of producer pitch: 92° softening point

Benzene.	Carbon Disulphide.	Chloroform	Carbon Tetrachloride.	Ether.		
19·5	22·4	27·2	28·35	37·23	32·87	40 times.
19·3	19·2	20·2	25·92	31·43	27·45	further 35 times, very pale.
17·8 (CS_2 final)	(C_6H_6 final)	19·83	24·42	21·48	16·07	Bad thimble, colourless.

Gooch Crucible Method.—The sample without sand was added little by little to 250 c.c. of hot solvent with constant shaking. It was boiled under a reflex condenser for 15 minutes, cooled, filtered, and washed about six times with fresh solvent until the filtrate became straw coloured; then with CS_2 until the extract had again become straw coloured; then twice with benzene to remove CS_2. The residue was dried for at least two hours at 100–105° C. When first treated with CS_2 and then benzene, the above procedure was reversed, but benzene was always the last to be used.

Vapour Extraction.—A thimble was suspended in vapour of boiling solvent under a reflux condenser and extracted until the filtrate became colourless.

Neutral Oil. A suitable oil was distilled and fraction between 180–200° collected, and washed with acid and alkali to free it from basic and acidic substances.

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[1] *Jour. Ind. and Eng. Chem.*, 1917, 9, 1100.

TABLE B.

No.	Material.	Benzene	Xylole.	Carbon Disulphide.	Carbon Tetrachloride.	Chloroform	Ether.	Pyridine.	Neutral Oil.	Gooch (C_6H_6 unless otherwise stated)	Vapour Extraction (C_6H_6 unless otherwise stated).
1.	Tar	(1) 1·64 (2) 1·7									
	Medium Soft Pitch, 62° C.	(1) 11·0 10·55 (CS_2 final) (2) 9·6 (hot extr.)	.	11·02 10·0 (C_6H_6 final)	14·48 13·88 (CS_2 final)	.				16·35 ..	17·42 14·40 (CS_2 final)
	Hard Pitch, 90° C.	(1) 19·3 17·78 (CS_2 final) (2) 31·38 (cold)		22·4 (40 times) 19·2 (CS_2 final)	(1) 24·6 (2) 25·92 24·42 (CS_2 final)	20·2 19·83 (CS_2 final)	(1) 21·48 (2) 22·95 16·0 (CS_2 final)		(1) 10·15 (2) 17·4	(1) C_6H_6, 31·2 32·8 (CS_2 final) 29·2 28·5 (2) CS_2, 29·2 (C_6H_6 final) 27·57	(1) C_6H_6, 22·02 (2) CS_2, 25·68 (C_6H_6 final) 22·9
2.	Tar	4·92		(1) 5·30 (2) 4·32 (probably slightly low)			5·98	4·38			
	Medium Pitch, 60·8° (Colman's still.)	17·43 15·18 (CS_2 final)	..	15·17 14·25 (C_6H_6 final)	21·45 20·03 (CS_2 final) 19·87 (C_6H_6 final)					22·3	23·7 22·67 (CS_2 final)
	Hard Pitch, 74° C. (Copper pot.)	14·52 12·2 (CS_2 final)	.	13·42				10·26		21·0	20·0
3.	Tar	...	.				.	.	.		9·1
	Medium Soft Pitch, Maker's Product	(1) 17·8 (2) 17·63 16·25 (CS_2 final)	.	(1) 16·53 (2) 17·23 15·73 (C_6H_6 final)					..	22·6	(1) 16·32 (2) 18·4 (3) 17·2
	Medium Soft Pitch, Maker's Product 72·3° (Copper pot).	24·45 21·25 (CS_2 final)	..	21·45		.	...	..	.	28·75	27·37
	Hard Pitch, over 90°. (Copper pot).	33·2 31·7 (CS_2 final)	30·92	...		..	..	..	...	35·04	30·82

The softening point of the pitch samples was taken by the "½" cube method.

From these figures it is to be seen that the best solvent, *i.e.* that leaving a residue most nearly approaching to "carbon," is pyridine, and that this has the disadvantage of having to be used in an all-glass apparatus. The second most desirable is the combined benzene-carbon disulphide solvent, employed as directed, and this it is that is recommended for general use. The remaining liquids have, relatively to the above, too little to recommend them.

CHAPTER VII.

AMMONIUM SULPHATE PLANT.

SULPHURIC ACID (B.O.V.)

Specific Gravity.—This is usually determined by means of a Twaddle's hydrometer, and reported in degrees Twaddle, which, however, can be calculated to specific gravity, each degree being equal to ·005 above the specific gravity of water (1·000).

Estimation of H_2SO_4.—The quantitative analysis of sulphuric acid is usually made by titrating a weighed quantity, it not being sufficiently accurate to measure the acid with a pipette or burette.

Weigh out 2 to 3 grams of the acid into a clean, dry, tared conical flask, dilute with 100 c.c. of distilled water and titrate with a "normal" solution of sodium hydrate, using methyl orange as indicator. Each c.c. of the normal soda solution contains 0·04005 gram NaOH and will neutralise 1 c.c. of normal sulphuric acid solution, containing 0·049 gram of H_2SO_4.

Example—2·250 grams of acid were taken, which required 30·5 c.c. of N/1 soda solution to neutralise it; therefore,

$$30{\cdot}5 \times 0{\cdot}049 = \text{weight in grams of } H_2SO_4$$

and

$$\frac{30{\cdot}5 \times 0{\cdot}049 \times 100}{2{\cdot}250} = 66{\cdot}42 \text{ per cent. } H_2SO_4.$$

Estimation of Arsenic.—For practical purposes the following crude test, if carried out on a "known" acid, may be used successfully, when testing a consignment of B.O.V. for its suitability for the manufacture of sulphate of ammonia, since the results are comparative with the practical results in the saturator.

Measure out 20 c.c. of the acid into a conical flask and dilute with 200 c.c. of distilled water. Add 0·5 gram zinc sulphide and shake for a few seconds; allow to settle, and examine. If only a slight turbidity the consignment may be safely used, but if a distinct precipitate is observed it should be rejected. Other impurities will come down with the arsenic in this test, but these are as detrimental as the latter.

For the accurate estimation of Arsenic, according to Lunge.—(a) Dilute 20 c.c. of the acid with water, and pass through it a stream of sulphur dioxide, until it smells strongly of the gas, in order to reduce the As_2O_5 to As_2O_3. (*Note.*—The gas should be passed for a considerable time to make sure of complete reduction.) Drive off the excess of SO_2 by heating and passing a current of CO_2, neutralise exactly with sodium carbonate and a little sodium bicarbonate, and titrate with decinormal iodine and starch. 1 c.c. of the iodine solution indicates 0·00495 gram As_2O_3. (Note any considerable proportion of iron should be previously removed.)

(*b*) *Marsh's Test.*—A special apparatus (fig. 36) is required. A is the evolution flask; B a tube containing calcium chloride to absorb moisture; and C a tube of hard glass attached to the drying tube. Into A place a few grams of zinc and 10 c.c. of pure dilute sulphuric acid (free from arsenic); allow the hydrogen to stream through the tube, then add 10 grams of the sample through the thistle funnel and wash down with water. At the same time place the bunsen into position, and heat the hard glass tube. The mirror obtained is then compared with standards.

(*c*) *Hager's Kramato Method*[1]—Into a porcelain basin 6 cms. in diameter, place 20 drops of acid and 40 drops of water. Treat this with 1·6 grams of finely powdered sodium bicarbonate, and if after stirring for five minutes any part of the $NaHCO_3$ remains undissolved, warm the mixture. Add 10 drops of ammonia and about 2 grams of ammonium oxalate, so that the acid is completely combined, this being absolutely necessary for the accuracy of the reaction. Then add 30 drops of hydrochloric acid to render it strongly acid. A brass plate should be scoured with sand and carefully dried, then place upon it one drop of the liquid, and warm it gently at first, then more strongly over a small flame. After washing the salt stain off, there will then be a spot left which will be grey to red or even black, according to the amount of arsenic present.

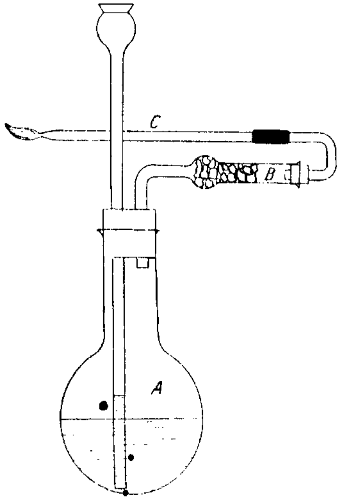

FIG. 36.

(*d*) *Hattensaur's Method.*[2]—500 c.c. of the sample are diluted with 500 c.c. of distilled water, to which 500 c.c of diluted hydrochloric acid (1 : 2) are added, the mixture being cooled. While still cold, sulphuretted hydrogen is passed through for one hour and the precipitated As_2S_3, which is free from lead, filtered and washed in a platinum or porcelain Gooch crucible. It is washed with hot alcohol to remove traces of sulphur, dried, and the As_2S_5 weighed. Instead of using the Gooch crucible, the precipitate may be washed and dissolved in 20 c.c. dilute (1:2) ammonia, the solution evaporated in a porcelain dish, and oxidised to arsenic acid which is estimated as ammonium magnesium arsenate.

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[1] According to Lunge in *Chem. techn. Untersuchungs-methoden*, vol. i. Berlin, 1899.

[2] *Zeitschr. f. angew. Chem.* 1896, 130.

Nitrous Acid (Blutcher).—For the quantitative determination of the nitrous acid, the sample should be titrated with potassium permanganate. The acid must always be added to the permanganate, never the permanganate to the acid. N/2 permanganate solution is diluted with five times the amount of warm water (30° to 40° C.) and the sulphuric acid is allowed to flow into it from a burette until the colour disappears. 1 c.c. N/2 permanganate solution equals 0·0095 gram N_2O_3.

SULPHATE OF AMMONIA.

Moisture.—The amount of free moisture is determined by drying a weighed quantity in a flat dish at 110° C. until the weight is constant, the loss in weight representing the moisture in the amount of sample taken.

Note.—Samples of sulphate of ammonia should always be kept in a stoppered bottle, so that no loss of moisture takes place.

Ammonia.—10 grams of the well-mixed sample is washed with distilled water into a 500 c.c. measuring flask; dissolved; the flask filled up to the graduation mark, and the whole well shaken. 50 c.c. of this solution are distilled with caustic soda solution in the distillation apparatus (fig. 3) into about 15 c.c of N/1 sulphuric acid.

Example— 50 c c. of solution taken (1 gram of sample).
15 c.c. N/1 H_2SO_4 after the experiment

required 1 c.c. of N/1 NaOH to bring it to neutral, then 15·0 − 1·0 = 14·0 c.c. N/1 H_2SO_4 used.

Now each c.c. of N/1 acid = 0·017 gram of ammonia;

therefore 14·0 × ·017 = ·238 gram NH_3 in 1 gram of the sample, or 23·80 per cent.

Free Acid.—10 grams of the sample are dissolved in 100 c.c. of distilled water. Methyl orange is added, and the solution is titrated with decinormal caustic soda solution, each c.c. of the solution = 0·0049 gram of sulphuric acid.

Iron Salts.—When, the ammonium sulphate is required for the manufacture of such explosives as ammonium perchlorate, the percentage of iron salts have to be estimated, since they cause a considerable amount of trouble during the filtering process.

10 grams of the sample are dissolved in distilled water, and the solution filtered To the filtrate and washings is added ammonia in excess which precipitates the iron, the latter being separated by filtration, washed, dried and weighed as Fe_2O_3 (ferric oxide).

AMMONIACAL LIQUOR.

In the following pages, tests by Linder, abstracted from the Fortieth Annual Report of the Chief Inspector of Alkali Works, are given, together with recent modifications.

Free Ammonia.—By distillation of 10 c.c. liquor (more if weak) diluted to about 300 c.c. in a round-bottomed flask, connected through a catch bulb to a Liebig's condenser, and receiver containing excess N/2 H_2SO_4 and provided with an outlet acid catch, packed with broken combustion tubing (some beads are found to yield alkali to N/2 acid, and their use is not recommended). At the close of the distillation, which requires about twenty minutes, air is blown through the apparatus to remove final traces of ammonia, and the excess of acid in the receiver is titrated with N/2 Na_2CO_3.

Fixed Ammonia.—Add boiled caustic soda solution in excess to the boiled liquor left in the flask, with sufficient water to replace that boiled off. Place a furthur definite quantity of N/2 H_2SO_4 in the receiver and proceed exactly as with Free Ammonia test.

Calculations.—

Percentage of free ammonia = 0·0085 × 10 × c.c. N/2 H_2SO_4 neutralised.
" " fixed " = 0·0085 × 10 " N/2 " "

Total Ammonia may be calculated by the addition of free and fixed ammonia, but should be estimated by distilling another 10 c.c. of the sample (diluted), together with excess of boiled caustic soda solution, into slightly more than the sum of the two amounts of N/2 H_2SO_4 neutralised in the two previous estimations, the excess acid being titrated back and the percentage of ammonia calculated as before. This serves as a check for the free and fixed ammonia.

Carbonic Acid (Linder).—10 c.c. of liquor are diluted to 400 c.c. 10 c.c. of ammoniacal calcium chloride (1 c.c. = 0·014 gram CO_2) are added, and the whole is heated in a stoppered bottle for 1½ to 2 hours in a water bath at 100° C. Cool somewhat, filter, wash by decantation through a filter with boiling water, and dissolve the calcium carbonate in a known quantity (25 c.c. to 50 c.c.) of N/2 HCl, with added cold water to prevent loss of acid. Titrate the excess of N/2 HCl with N/2 Na_2CO_3. The small amount of calcium carbonate on the filter is best recovered by incineration in a tared capsule.

Calculations.—Grams of CO_2 per 100 c.c. of liquor = 0·011 × 10 × c.c. of N/2 HCl neutralised.

Modification by Dr. H. G. Colman[1]—10 to 25 c.c. (according to the amount of CO_2 present) is run from a pipette into a hot solution of calcium chloride, avoiding as far as possible exposure to the air (from which the solution absorbs carbon dioxide). The beaker is covered and heated until the precipitated calcium carbonate granulates.

This is then filtered and washed, the precipitated calcium carbonate dissolved in 25 c.c. of N/1 HCl, the unused hydrochloric acid being determined by titration with N/1 caustic soda, using methyl orange as indicator. (1 c.c. of N/1 HCl = 0·0022 gram of CO_2.)

Chloride (Linder).—10 c.c. of boiled liquor (for convenience 250 c.c. are boiled to expel sulphide, etc., cooled and made up to 250 c.c. for estimation of chloride, sulphocyanide, ferrocyanide, etc.,) are diluted to 150 c.c., 20 c.c. of hydrogen peroxide (10 volumes free from chloride) are added, and the solution boiled down until the brown colour has almost entirely disappeared; 10 to 15 drops of potassium chromate solution are then added to destroy the excess of peroxide and to aid in the removal of organic matter, and the boiling continued for five minutes. Filter if necessary from traces of green chromium hydrate, cool, neutralise by the addition of a pinch of sodium bicarbonate, and titrate with N/10 $AgNO_3$.

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[1] *J.S.C.I.*, Dec. 1918.

Calculation.—

HCl in grams per 100 c.c. = ·00364 × 10 × c.c. N/10 $AgNO_3$ used.

Another method is to evaporate 50 c.c. of the liquor to dryness on the water bath; add water, and filter off the tarry matter. Mix the filtrate with a solution of copper sulphate and ferrous sulphate in about equal proportions, and filter the liquid again. Add nitric acid and silver nitrate to the filtrate and boil; allow the precipitate to settle, and pass the supernatant liquid through a filter. Before finally filtering off the precipitate (silver chloride), digest it several times with hot nitric acid to dissolve out the silver sulphide resulting from the decomposition of the silver thiosulphate. Filter off the silver chloride, and weigh.

Sulphur.—(*a*) *As Sulphate* (*Linder*). 250 c.c. of the liquor is concentrated to about 10 c.c. on the water bath, 2 c.c. of strong hydrochloric acid added, and the evaporation continued to dryness to decompose thiosulphate and render organic matter less soluble in water. The residue is extracted with water, and the filtered solution made up to 250 c.c. The sulphate is determined by precipitating 100 c.c. of this solution with barium chloride, allowing the precipitate one night to settle.

The amount of oxidation undergone by the thiosulphate under these conditions is insignificant.

Calculation.—

Sulphur as sulphate, grams per 100 c.c. = 0·1373 × gram $BaSO_4$.

Another method is to evaporate 250 c.c. of liquor to dryness; add water, filter off the organic matter, and boil the solution with hydrochloric acid; add a little zinc oxide and filter the liquid. Precipitate the sulphates with barium chloride and treat as in Linder's method.

(*b*) *As Sulphocyanide* (*Linder*).—To 50 c.c. of the boiled solution (see "Chloride") add ferric chloride in amount slightly in excess of that required to complete the precipitation of the ferrocyanide.—(*Note*—As ferrocyanide has only been detected in gas liquors on very rare occasions, addition of ferric chloride is generally found to be unnecessary, and is omitted, the appearance of prussian blue, however, on adding ferric chloride, slightly acid, to the boiled liquor is regarded as one of the best qualitative tests for ferrocyanide)—as prussian blue; filter (the solution may be warmed to promote the separation of the blue in the flocculent condition essential for rapid filtration), cool, add sulphurous acid in sufficient excess, followed by copper sulphate, and set aside in stoppered flask for one or two hours in the cold, to deposit the cuprous salt. Filter cold, wash thoroughly with hot water, using a little sodium sulphate in the wash water if the precipitate shows a tendency to pass through the filter paper; the final washings must remain colourless on addition of a trace of ammonium sulphide. Wash the cuprous sulphocyanide, which should be white, back into the flask, the last traces being removed from the paper by warming on a clock-glass with dilute nitric acid (1 : 3); add 1 c.c. to 2 c.c. of strong nitric acid, and boil the solution until green (in presence of much organic matter, evaporation to dryness and gentle ignition followed by furthur treatment with nitric acid is sometimes required to complete the oxidation of the copper); cool the oxidised liquid, add slight excess of sodium carbonate, acidify with acetic acid, add potassium iodide, dilute, and titrate the liberated iodine with N/10 thiosulphate, using starch as indicator.

Calculation.—Sulphur as sulphocyanide, grams per 100 c.c. = 2 × 0·0032 × c.c. of N/10 thiosulphate required.

(*c*) *As Sulphide, Sulphite, and Thiosulphate* (*Linder*).—(1), 10 c.c. of liquor is diluted to 500 c.c., acidified with hydrochloric acid, and titrated with N/10 iodine solution, using starch as indicator. The volume of N/10 iodine required determines that of the liquor taken for (2).

(2), 10 c.c. or more is added to excess of ammoniacal zinc chloride solution diluted to about 80 c.c. with warm water (40°–50° C.).

Sulphide.—The zinc sulphide on the filter is washed into excess of iodine, acidified with hydrochloric acid (the last traces of sulphide being washed through with cold dilute acid) after vigorous agitation to complete the solution of the zinc sulphide, water is added, and the excess iodine determined with N/10 thiosulphate.

Calculation.—Sulphur as sulphide, grams per 100 c.c.
= 10 × 0·0016 × c.c. N/10 iodine required.
H_2S = 10 × 0·0017 × c.c. N/10 iodine required.

Sulphite and Thiosulphate.—The conclusion is reached that no exact estimation of sulphite and thiosulphate is possible in ammoniacal liquors by any method based on titration with N/10 iodine except in quite exceptional cases. A united figure for these two constituents can be reached by difference, subtracting from the total sulphur, found by bromine oxidation, the sum of the sulphurs present as sulphate, sulphocyanide and sulphide. According to Colman, an approximate estimation of ammonium thiosulphate is obtained from the number of c.c. of N/10 iodine solution required by 10 c.c. of the liquor after treatment with cadmium chloride. Each c.c. of iodine = 0·0148 gram $(NH_4)_2S_2O_3$. The results, however, tend to be slightly high, owing to the other impurities, such as the thiocyanate and phenols having some action on the iodine.

The following is a rapid method (also by Colman) for the estimation of hydrogen sulphide in more concentrated liquors:[1]—10 c.c. of the sample is added to 50 c.c. of N/10 iodine solution, mixed with more than enough hydrochloric acid to neutralise the whole of the ammonia, and the unused iodine titrated with N/10 thiosulphate and starch, the difference giving the iodine used. A further 10 c.c. is then treated with cadmium chloride to remove all hydrogen sulphide, and after filtering through pulp, added to 10 c.c. N/10 iodine and hydrochloric acid, titrating back with N/10 thiosulphate. The amount of iodine used, which represents that taken up by substances other than hydrogen sulphide, is deducted from the amount of iodine found in the first test, the difference giving the number of c.c. of N/10 iodine corresponding to the hydrogen sulphide in 10 c.c. of the liquor.

(1 c.c. of N/10 iodine = 0·0017 gram H_2S).

Total Sulphur.—50 c.c. (100 c.c. of weaker liquors) of liquor are delivered drop by drop from a burette into a flask, containing excess of bromine (free from sulphur), covered by water strongly acidulated with hydrochloric acid. The oxidised solution is evaporated to dryness on the water bath, the residue repeatedly extracted with boiling water, filtered, cooled, made up to 250 c.c. with water, and 100 c.c. of the solution precipitated with barium chloride.

Sulphur, grams per 100 c.c. = 5 × 1·373 gram $BaSO_4$. Coke-oven liquors on oxidation with bromine often yield a heavy yellow precipitate of brominated phenols; this may retain traces of sulphur in amount sufficient to affect the percentage distribution sulphur figures, unless it is recovered by fusion with potassium carbonate and nitrate and included in the total.

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[1] *J.S.C.I.* Dec. 1918.

Sulphur as Polysulphide.—With respect to this estimation three methods have been tried.

(1) The liquor is mixed with excess of a solution of ammonium cyanide of known strength in a stoppered bottle or flask, and the excess of cyanide remaining after conversion of the polysulphide into thiocyanate determined by distillation.

(2) The liquor is treated as above; but in this case the thiocyanate formed is determined. The thiocyanate equivalent of the polysulphide present is then obtained by deducting from the total thiocyanate figure the amount of thiocyanate originally present in the liquor separately determined.

(3) The liquor is slightly acidified with hydrochloric acid, neutralised with ammonium carbonate, warmed to promote coagulation of the separated sulphur and tarry matter, and the precipitate collected on a Gooch crucible, dried, and weighed. The proportion of sulphur present in the impure product is then determined by precipitation as barium sulphate after oxidation. None of these methods are, however, free from criticism. Nos. 1 and 2 are subject to interference from dissolved oxygen as already stated, which, unless excluded, causes the polysulphide figure to exceed its proper value. In method No. 3 sulpho compounds of a tarry nature are apt to be precipitated co-jointly with the sulphur and yield sulphate on oxidation with fuming nitric acid or sodium peroxide. Of the three methods No. 2 appears to offer the most advantages.

Example—Liquor contains per 100 parts.

Sulphuretted hydrogen, ...	0·945
Sulphur as thiosulphate, ...	0·09
Hydrocyanic acid, ...	Nil.

25 c.c. potassium cyanide solution (2 grams KCy) neutralised with sulphuric acid and 20 drops ammonia added. 100 c.c of the liquor added, and the mixture diluted to 250 c.c and allowed to stand 10 to 15 minutes. 50 c c. boiled to remove ammonia. 15 c.c. iron alum added, filtered, and the thiocyanate precipitated as cuprous salt, etc. (See Sulphur B.)

Example—

	Per 100 c.c. liquor.
N/10 $AgNO_3$ (*a*) 33·0, (*b*) 33·2 } mean $33·1 \times 5 =$.	165·5 c.c.
Deduct equivalent of thiocyanate present in liquor .	125·1 „
	40·4 „

Whence

Sulphur as polysulphide per 100 c.c. liquor $= 40·4 \times 0·0032 = 0·129$ gram.

Sulphites.—The difficulties attending an exact estimation of sulphite in ammoniacal liquors have been carefully considered by Linder in the hope of elaborating a reliable method for detecting and estimating this important constituent, the following method being adopted:

The Polysulphide Method.—It is a well established fact that solutions of ammonium polysulphide and ammonium sulphite react to form ammonium sulphide and ammonium thiosulphate.

$$(NH_4)_2S_2 + (NH_4)_2SO_3 = (NH_4)_2S + (NH_4)_2S_2O_3$$

As a result of this reaction the iodine value of the solution is decreased by 1 c.c. N/10 iodine for every 0·0032 gram of sulphur as sulphite decomposed, the iodine value of the thiosulphate produced being half that of the sulphite reduced. This decrease affords a means, therefore, of calculating the amount of sulphite present.

The procedure adopted is as follows :—

a. Total iodine value of solution is determined by titrating 10 c.c. of diluted and acidified liquor with N/10 iodine.

N/10 iodine equivalent of $H_2S + H_2SO_3 + H_2S_2O_3$ = A c.c.

b. Iodine equivalent of sulphide is determined by ammoniacal zinc chloride method.

N/10 iodine equivalent of H_2S = B c.c.

Then N/10 iodine equivalent of $H_2SO_3 + H_2S_2O_3$ = A − B c.c.

c. Iodine equivalent of half the sulphite + the thiosulphate is determined by adding 10 c.c. of liquor to 10 c.c., or more, of diluted polysulphide liquor (prepared by digesting strong ammonium sulphide solution with powdered sulphur, decanting ; 2 c.c. of this solution freshly diluted to 100 c.c. gives the dilute solution used for analysis).

After standing 5 to 10 minutes in the cold, the clear yellow liquid is precipitated by excess of ammoniacal zinc chloride and filtered. The filtrate is acidified with hydrochloric acid and titrated with N/10 iodine.

N/10 iodine (less iodine for thiosulphate contained in the polysulphide used) is the equivalent of

$\frac{1}{2}H_2SO_3 + H_2S_2O_3$ = C c.c.

Two examples will make this clear :—

1. *Coke-Oven Liquor*—

10 c.c. liquor,	$H_2S + H_2SO_3 + H_2S_2O_3$	8·57 c.c. N/10 iodine .	(A).
10 c.c. liquor,	H_2S . . .	7·71 ,, ,, ,,	(B).
	$H_2SO_3 + H_2S_2O_3$.	0·86 ,, ,, ,,	(A − B).
10 c.c. liquor,	$\frac{1}{2}H_2SO_3 + H_2S_2O_3$.	0·60 ,,	{Thiosulphate in polysulphide deducted (C).
	$\frac{1}{2}H_2SO_3$ . .	0·26 ,,	N/10 iodine A − (B + C).

Whence

Sulphur as sulphide = 10 × ·0016 × 7·71 = 0·1234 gram sulphur per 100 c.c.
,, ,, sulphite = 10 × ·0016 × 2 × 0·26 = 0·0083 ,, ,, ,, 100 ,,
,, thiosulphate = 10 × ·0016 × 0·34 = 0·0218 ,, ,, ,, 100 ,,

2. *Gas Liquor*—

10 c.c. liquor,	$H_2S + H_2SO_3 + H_2S_2O_3$	32·13 c.c. N/10 iodine	(A).
10 c.c. liquor,	H_2S . . .	30·71 ,, ,, ,,	(B).
	$H_2SO_3 + H_2S_2O_3$.	1·42 ,, ,, ,,	(A − B).
10 c.c. liquor,	$\frac{1}{2}H_2SO_3 + H_2S_2O_3$.	1·33 ,, ,, ,,	(C).
	$\frac{1}{2}H_2SO_3$.	0·09 ,, ,, ,,	(A − (B + C).

Whence

Sulphur as sulphide = 10 × ·0016 × 30·71 = 0·4914 gram S per 100 c.c.
,, ,, sulphite = 10 × ·0016 × 2 × 0·09 = 0·0029 ,, ,, ,,

Sulphite, if present, only exists in this liquor in insignificant amount. It is reasonable to conclude that it is absent.

It should be pointed out that the iodine figure for $\frac{1}{2}H_2SO_3$ is reached by subtraction = A − (B + C). This will eliminate, to a material extent, the effect due to interference of organic matter, as titrations A and C are carried out under very similar conditions, while B is not considered to be materially affected under the conditions observed for precipitation of the zinc sulphide.

Distribution of Sulphur in Ammoniacal Liquor.—If we subtract from the total sulphur found by bromide oxidation the sum of the constituent sulphurs found as sulphate sulphocyanide, thiosulphate (determined by titration of the acidified filtrate, from the sulphide by N/10 iodine) and sulphide, a difference figure is obtained, which has proved to be invariably negative in sign, since the adoption of the improved method for estimating sulphocyanide. Evidence had been obtained that some of the difference noticed was due to the presence of sulphite, which caused the thiosulphate figure to largely exceed its proper value, by reason of the factor for conversion of N/10 iodine into sulphur as thiosulphate being 0·0064 gram sulphur per 1 c.c. N/10 iodine, while that for sulphite is only one-fourth of this. This has failed, however, to reduce the difference figure to the limits of experimental error, and the conclusion is reached, therefore, that organic matter is the disturbing cause, as such differences are not noticed when the same methods are applied, to determine the same constituents, in solutions from which organic matter is excluded. Various considerations point to the thiosulphate titration as the one peculiarly liable to such interference; for this reason the iodine method of estimating this constituent in ammoniacal liquors is finally rejected, in favour of a figure arithmetically obtained by difference.

Cyanide (Hydrocyanic Acid).—According to the Fifty-fourth Annual Report of the Chief Alkali Inspector, hydrocyanic acid in ammoniacal liquor of ordinary strength is conveniently determined by means of Feld's method, whereby 50 to 100 c.c. of the liquor are distilled with excess of lead nitrate into 25 c.c. of normal soda and the distillate titrated with N/10 silver nitrate, with the addition of a crystal of potassium iodide as indicator. The method is inapplicable, however, for the analysis of liquor of high strength, as the amount of lead nitrate required to saturate the solution then becomes inconveniently great, and the liquor in the flask too highly charged with precipitate to admit of safe distillation. The cyanide in such liquors is more conveniently determined by the "Polysulphide" method, whereby cyanide is converted into thiocyanate by the action of ammonium polysulphide, and titrated with silver nitrate. The amount of thiocyanate and chloride pre-existing in the liquor is determined by a blank experiment and deducted.

The following procedure is recommended in the case of liquor containing a small amount of chloride:

(1) *Blank Experiment.*—50 c.c. of the liquor are run into 100 c.c. of boiling water in a flask, and the boiling continued to expel ammonia; 10 c.c. of a saturated solution of iron alum are then added to the hot liquor, and the solution allowed to stand 5 to 10 minutes; it is then filtered, and the precipitate washed with hot water. To the cold filtrate 5 c.c. of 50 per cent. nitric acid are added, and the solution nitrated with N/10 silver nitrate. A sufficient excess of the silver solution (0·5 to 1 c.c.) should be added to ensure

precipitation of all the chloride, and the solution filtered and brought back with N/10 ammonium thiocyanate.

(2) *Conversion of Cyanide into Thiocyanate.*—100 c.c. of the liquor are run into 50 c.c. of water, containing sufficient ammonium polysulphide to convert the whole of the cyanide into thiocyanate (say 0·1 sulphur as polysulphide per 0·05 HCγ) and the mixture diluted to 250 c.c. and allowed to stand 10 to 15 minutes. 100 c.c. of the mixture—which should be yellow in colour—is then boiled to remove ammonia (10 to 15 minutes), with addition of more water if required. To the hot solution add 10 c.c. iron alum and proceed as above. The following are cited by way of illustration :—

Concentrated liquor of approximate composition—

Ammonia, ...	22·0 per cent.
Sulphuretted hydrogen, .	0·3 „ „

Blank.—50 c.c. of liquor require 1·42 c.c. N/10 $AgNO_3$ for chloride, plus thiocyanate = 2·84 c.c. per 100 c.c. liquor.

Polysulphide mixture.—100 c.c. liquor, 2·5 polysulphide (=0·1 gram available sulphur) made up to 250 c.c.

100 c.c. require (*a*) 4·56 } mean 4·53 c.c. N/10 $AgNO_3$.
„ „ (*b*) 4·50 }

Whence 100 c.c. require 4·53 × 2·5 = 11·30 c.c. N/10 $AgNO_3$.
deduct blank = 2·84 „ „ „
8·46

Whence

Hydrocyanic acid per 100 c.c. liquor = 8·46 × 0·0027 = 0·0228 gram.

With liquors highly charged with chloride it is necessary to precipitate the thiocyanate as cuprous salt, as in the following estimation of thiocyanates: 60 to 70 c.c. of distilled water are raised to the boil in a suitable flask and the boiling continued for a few minutes to expel dissolved oxygen, 50 c.c. of the liquor under examination are then slowly run into the freely boiling water, and the boiling continued for 10 to 15 minutes to expel ammonium cyanide and sulphide. To the hot solution (90° - 95° C.) are added 10 c.c. of a saturated solution of ammonium iron alum to precipitate ferrocyanides and oxidise thiosulphate to tetrathionate, a sufficient excess being used to convert the thiocyanate into the blood-red iron salt. After standing 5 to 10 minutes the solution is filtered, first by decantation and subsequently by washing with boiling water. To the still warm filtrate acid sulphite of soda is added, followed by a distinct excess of a 10 per cent. solution of copper sulphate and the solution allowed to stand, say for half an hour at 50° – 60° C., to coagulate the cuprous thiocyanate. The solution is then filtered and the precipitate thoroughly washed with boiling water until the final washings remain colourless on addition of a dilute solution of potassium ferrocyanide. The residue in the filter is then washed back into the flask and digested with 25 c.c. of a 4 per cent. solution of caustic soda (free from chloride) at 30° – 40° C. It is then filtered, and the filtrate acidified with 5 c.c. of nitric acid (50 per cent. strength) and titrated with N/10 silver nitrate, with addition of 1 c.c. of a saturated solution of iron alum as indicator. In some cases filtration of the acidified solution is called for before titration, and, in general, the end point is rendered sharper, if a slight excess of the silver solution is added (say 0·5 c.c.) and the solution filtered and titrated with N/10 ammonium thiocyanate.

Sulphur as thiocyanate, gram per 100 c.c. = 2 × ·0032 × c.c. N/10 $AgNO_3$.
Hydrocyanic acid, gram per 100 c.c. = 2 × ·0027 × c.c. N/10 $AgNO_3$.

Colman[1] recommends the following method for concentrated liquors:—100 c.c. of the liquor is taken, if possible directly from the bulk to be analysed; if not, from a sample taken and preserved from contact with air as much as possible, and slowly run from the pipette into a flask containing about 150–200 c.c. of boiling water, to which about 10 c.c. of N/1 caustic soda has been added. The water in the flask should have boiled for some minutes before the addition of the sample, so as to ensure the removal of all dissolved oxygen. When the bulk of the ammonia has been driven off, a solution of 5 grams of lead nitrate is added, and the mixture distilled for 20–25 minutes; the distillate is collected in water containing 25 c.c. N/1 caustic soda, the end of the condenser dipping beneath the surface of the liquid in the receiver. All hydrocyanic acid present as ammonium cyanide is found in the distillate, which is titrated with N/10 silver nitrate in the usual manner, adding a little potassium iodide as indicator (1 c.c. N/10 $AgNO_3$ = 0·0054 grams H.C.N.

Colman's test for Ammonium Ferrocyanide and Thiocyanate.—A few drops of ammonium polysulphide solution are added to 100 c.c. of the sample till the solution shows permanently the yellow polysulphide colour, whereby any cyanide present is converted into thiocyanate. After standing about 15 minutes lead carbonate is added to remove hydrogen sulphide, and the filtrate boiled with addition of about 10 c.c. of N/1 caustic soda till most of the ammonia is driven off. The addition of a fixed alkali before boiling is necessary, as ammonium ferrocyanide loses part of its hydrocyanic acid when its solution is boiled, and the previous removal of hydrogen sulphide is necessary, as in the presence of ammonium sulphide, hot alkali causes a partial conversion of ferrocyanide into thiocyanate, thereby rendering the results for the former too low, and for the latter correspondingly high.

The solution is made *slightly* acid with sulphuric acid, and a solution of ferric alum added drop by drop till it shows the distinctive colour of ferric thiocyanate. The solution is then filtered through pulp, which retains the prussian blue formed from the ferrocyanide, and is washed with water containing some dissolved electrolyte, such as sodium or potassium sulphate (washing with distilled water often causes some colloidal prussian blue to pass through the filter). The precipitate contains all hydrocyanic acid present as ferrocyanide, and the filtrate all that is present as thiocyanate. (With small amounts of ferrocyanide, it frequently happens that the colour of ferric thiocyanate makes it difficult to see whether any prussian blue has been precipitated, but this shows up distinctly on the filter-paper pulp after washing. Filtration should be carried out in all cases, as even quantities of prussian blue which cannot be estimated, if left in, interfere with the end reaction in the subsequent titration of the filtrate for thiocyanate).

About 10 c.c. of normal caustic soda is poured on to the filter-paper pulp, containing the prussian blue, which decomposes it, forming sodium ferrocyanide. This is washed out with water, the filtrate strongly acidified with sulphuric acid, and distilled according to the method of H. E. Williams, with the addition of a little cuprous chloride, when all the hydrocyanic acid distils over, and is collected in water containing about 25 c.c. of N/1 caustic soda, as in the determination of the cyanide, the distillate being similarly titrated with N/10 silver nitrate. A convenient method is to use a 10 per cent. solution of cuprous chloride in hydrochloric acid, some copper strips being kept in the bottle to maintain the whole in the cuprous state.

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[1] *J.S.C.I.*, Dec. 1918.

Two alternative methods may be employed for estimation of the thiocyanate in the filtrate from the prussian blue, the first being the quicker but rather less accurate for an unpractised eye.

The first method consists in adding to the filtrate a further quantity of ferric alum, heating to 95° C., and after 5 minutes, cooling well, then adding dilute nitric acid (free from nitrous and hydrochloric acids), and titrating by Volhard's method with N/10 silver nitrate until the red colour of the ferric thiocyanate disappears (1 c.c. of N/10 $AgNO_3 = 0{\cdot}0027$ gram HCN, or 0·0076 gram NH_4CNS). The solution in this case does not become colourless, but almost always retains a pink colour, due to the action of the ferric salts upon the phenols present, and this makes the end point of the titration rather less easy to decide, but with a little practice there is no difficulty in ascertaining the point where the colour due to ferric thiocyanate disappears.

To obviate this difficulty entirely, the second method which affects the removal of the phenols and other impurities present is preferable, until experience has been gained in the titration by the first method. This method must always be employed if chlorides are present. In it, the filtrate from the prussian blue, which should be only slightly acid, is heated to boiling with the addition of more than sufficient sodium sulphite to reduce the whole of the ferric salt present to the ferrous state. If a large excess of ferric alum has been used for precipitation of the ferrocyanide, a correspondingly large amount of sulphite is required. Copper sulphate solution is then added in excess and the precipitated cuprous thiocyanate filtered through pulp, washed, and the pulp and precipitate stirred with a hot solution of caustic soda or sodium carbonate (free from chlorides) and filtered. The addition of a few drops of ferric alum solution to the alkaline solution (forming ferric hydroxide) often facilitates the filtering and washing of the mixture through pulp. The well-cooled filtrate is then acidified with dilute nitric acid (free from nitrous and hydrochloric acids), ferric alum added as indicator and the titration with N/10 $AgNO_3$ made as before, until the colour of ferric thiocyanate disappears, the solution now becoming completely colourless. If the amount of cyanide has been previously estimated, the amount found must be deducted from that found as thiocyanate, as this figure includes all hydrocyanic acid present as cyanide in the original sample owing to the preliminary treatment specified with ammonium polysulphide.

CHAPTER VIII.

CALORIMETRY AND PYROMETRY.

General Remarks.—It is often of greater importance to know the comparative calorific values of fuels than the absolute figure. Thus, if a purchase of coal were being made, and a series of samples submitted to a test, the one giving the highest calorific value—other things being equal—would be the most economical. The quantity of ash and sulphur, the ease or difficulty of burning, the cost, etc., would also be taken into consideration; but comparative heat values would be of equal service to a figure absolutely correct. This would also be the case if it were desired to discover whether coal from a given source varied in quality from time to time.

No calorimeter for fuels, however elaborate and costly, yields absolutely correct calorific values. All are restricted in this respect by the delicacy of the thermometer with which the temperature is read. Any instrument, therefore, which yields concordant results, with a close approximation to accuracy, is of equal service to the most expensive forms. For all ordinary purposes, Darling's calorimeter, used with the glass vessel, suffices. If for any reason it is desired to obtain a figure closer to the absolute value, the copper vessel and shield made for the purpose should be used, and also a more delicate thermometer.

Calorific values are sometimes expressed as (1) calories per gram of fuel; (2) pound-degree Centigrade heat units per pound of fuel; and (3) British thermal units, or pound-degree Fahrenheit units per pound of fuel. The figures for (1) and (2) are identical; and (3) may be obtained by multiplying (2) by $\frac{9}{5}$.

Thus, if 1 gram of coal gives 8250 calories or gram – ° C. units, then one pound of coal will give 8250 pound – ° C. units, or $8250 \times \frac{9}{5} = 14,850$ British thermal units.

The *evaporative power* of a fuel expresses the number of pounds of water at the normal boiling point 100° C. or 212° F. which would be converted into steam at the same temperature by burning one pound of the fuel. It is obtained by dividing the calorific value by the number representing the latent heat of steam, which for Centigrade units is 537, and for Fahrenheit units 967.

Thus, in the above case $\frac{8250}{537}$ or $\frac{14,850}{967} = 15{\cdot}36$.

Evaporative power = 15·36.

The "Darling" Fuel Calorimeter (fig. 37).—(1) Carefully grind up an average sample in an iron mortar, and weigh out 1 to 1·5 grams in the crucible. Brush any particles from the sides into the mass at the bottom.

(2) Prepare a quantity of water at a temperature about 2·5° C. below the temperature of the room. Water drawn from a tap varies in temperature according to the season; but usually it will be necessary to add a little warm water to it in order to bring it to the requisite temperature. Measure out 1400 c.c. into the vessel.

(3) Place the crucible in position, and fasten the glass cover down upon the rubber ring by means of the screws, so as to form an airtight joint. The screws must only be turned until a resistance is felt; any further tightening might crack the glass cover.

(4) Insert the rubber cork into the neck so that the ignition-wire is embedded in the fuel. The copper wire should terminate about level with the rim of the crucible, and the tube delivering the oxygen about ½ inch above the surface of the fuel.

(5) Turn on a gentle stream of oxygen from a cylinder or gas holder, and immerse the apparatus in the water. Carefully note the temperature of the water, and complete the battery circuit. As soon as the fuel is ignited, disconnect the battery. Allow the combustion to proceed steadily until completed, then continue passing the oxygen, mixing the water by lifting the combustion arrangement up and down, until no further rise of temperature is observed. Note the temperature carefully.

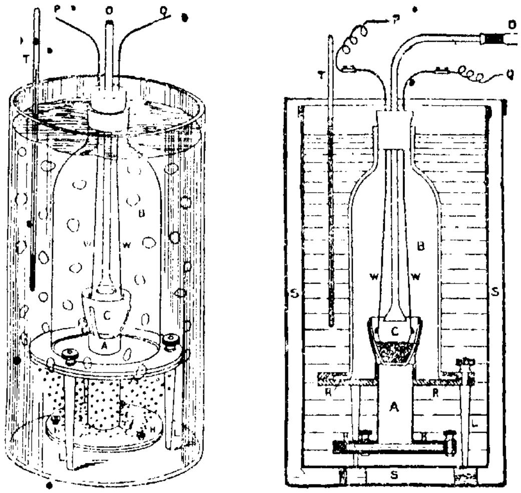

FIG. 37.

Precautions.—(*a*) The oxygen must never be admitted so rapidly as to cause particles to be blown out of the crucible. The time required to burn 1 gram of average coal in a steady stream of oxygen is about 5 minutes.

(*b*) If the sample is observed to burn with a smoky flame, the combustion must be stopped, as the result will be valueless owing to unburnt carbon. A second combustion should then be performed with the end of the oxygen tube one inch below the cork until all volatile matter has burnt off, after which the tube may be pushed down to the crucible and the combustion completed.

(*c*) During the combustion the tube delivering the oxygen should be moved about so as to ensure that every particle of coal is consumed. The flexibility of the rubber cork allows of this operation being easily performed. In every case near the end of the combustion, the supply of oxygen should be sufficient to cause the crucible to become visibly red-hot, whereby complete combustion is secured.

(6) The calorific value is calculated as follows:—

$$\frac{(\text{Weight of water} + \text{water equivalent}) \times \text{rise of temperature}}{\text{Weight of fuel taken}} = \text{cal. value.}$$

1 cubic centimetre of water is taken as weighing 1 gram. If a Fahrenheit thermometer is used, the result will express British thermal units per pound of fuel; if Centigrade readings are taken, the figure will represent either calories per gram or pound-degree C. units per pound.

Example— 1 gram of Welsh steam coal burnt as above.
Water taken = 1400 c.c. or grams.
Water equivalent of apparatus and vessel = 204 grams.

Temperature of water before combustion = 14° C.
Temperature of water after combustion = 19·20° C.
Temperature of room = 16·6° C.
Calorific value =

$$\frac{(1400+204)\;(19{\cdot}20-14)}{1} = 8341 \text{ cals. per gram,}$$

or 8341 lb.-° C. units per pound.

$$8341 \times \frac{9}{5} = 15{,}014 \text{ British thermal units per pound.}$$

$$\text{Evaporative power} = \frac{8341}{537} = 15{\cdot}53.$$

The "Bomb" Calorimeter.—This type of calorimeter is the nearest to perfection and lends itself to the ultimate analysis of the fuel at the same time.

The bomb (fig. 38) is usually made of steel, and is lined with enamel or nickel, or for very accurate work with gold or platinum. It is provided with a tightly fitting cover, held firmly in place on the gasket by a collar screwed down on the outside. Through a valve in the cover oxygen is admitted for combustion. The capsule in which the coal is placed for combustion is supported, near the centre of the bomb, on one of the electrodes, which in turn is attached to the cover. The other electrode pierces the cover and is insulated from it. The bomb stands in a calorimeter vessel containing a weighed quantity of water (usually about 2000 grams). Midway between the bomb and the side of the vessel an accurate thermometer, which, with the aid of a cathetometer and telescope may be read to thousandths of a degree, is introduced through the cover of the calorimeter and fixed in place with the bulb of the thermometer opposite the centre of the bomb. While a determination is being made, the water is thoroughly stirred at a uniform rate with a stirrer which projects through a hole in the cover. The air space between the inner and outer pails serves as an insulation from the heat of the room. For accurate work this space is also filled with water, and in that case it also is provided with stirrer and thermometer.

Formula for Calorific Power:—

$$C = \frac{r(W+w) - (\cdot238\ N + 2a + 1{\cdot}6\ F)}{S}$$

C = calories produced by burning 1 gram.
r = corrected rise in temperature.
W = the weight of water in the calorimeter in grams.
w = the water value of the calorimeter.
N = mgms. of nitric acid formed.
a = mgms. of sulphuric acid formed.
F = mgms. of iron wire (used for ignition) burnt.
S = weight of the sample of coal burnt.

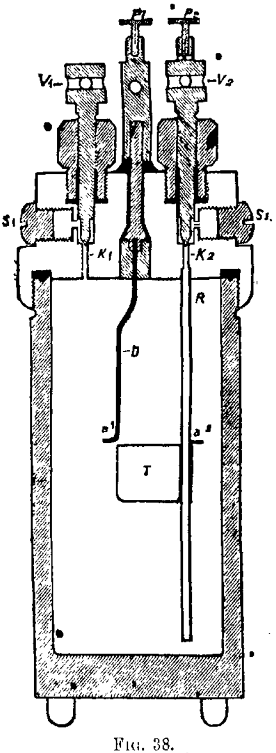

FIG. 38.

The acids being estimated after the test by chemical means.

In the modification by Dr. K. Kroeker there are entrance and exit tubes, by means of which a current of dry air may, after the experiment, be passed through the bomb, and the escaping gases and water vapour collected in the usual weighed calcium chloride tubes and potash bulbs, allowing for the determination of the water and, if desired, of the carbon dioxide produced in the combustion.

CALORIFIC VALUE OF GASES.

Junker's Calorimeter (fig. 39).—This calorimeter is made of copper, and consists of a combustion chamber surrounded by a water-jacket, passing vertically through which are a number of tubes open at both ends. Surrounding this water-jacket is another jacket, which forms an air space to prevent loss of heat by radiation. The water, after passing through the inlet funnel (provided with an overflow to keep the head of water constant), flows through a regulating cock and over the bulb of the inlet thermometer. Thence it circulates around the vertical tubes previously mentioned, and, becoming heated by the products of combustion, rises and flows past a series of baffle plates and an outlet thermometer to the outlet funnel. From there it is conveyed by a piece of flexible rubber tube either to a measuring cylinder or to waste—the tubing being manipulated by hand. The gas, after passing through the governor and meter, is burnt in a bunsen burner, and the products of combustion, rising up through the combustion chamber, are deflected at the top and fall down through the vertical tubes—the latter communicating their heat to the water circulating around them. The products issue through a large tube provided with a regulating valve. Any condensed water is led away by a tube, collected and measured; the amount collected enabling a correction to be made for the latent heat of the steam generated during the combustion of the gas.

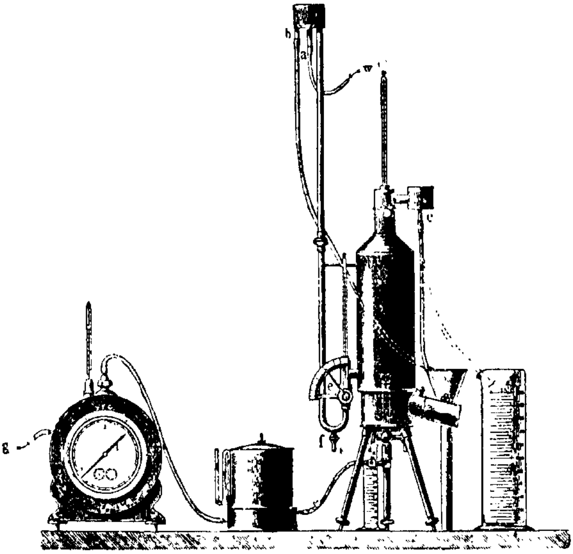

FIG. 39.

The apparatus is used in the following manner:—After the thermometers have been put into position the water is turned on by the cock (f), and when it is running from both overflows the gas is lit and burned at the rate of from 6 to 8 cubic feet per hour. The temperature of the water at the outlet will begin to rise until a temperature is obtained at which it will remain constant. The speed of the water passing through the apparatus is then regulated by the cock (f), so that there is a difference in temperatur between the inlet and outlet thermometers of 10° to 20° C. As soon as th difference is nearly constant and the condensed water is dripping regularl from the pipe (d) the test is commenced. Wait until the index of the ga meter, which registers the gas consumed by the flame, passes any particula point, and then rapidly move the hot water over from the funnel to th measuring cylinder and place a small measuring cylinder under the condense water outlet. The readings of both thermometers are taken every minute the test being continued until about one cubic foot of gas has passed, and th measuring cylinder, which should be of sufficient size, is filled to the mark when the meter is read, the warm water tube connected to waste, and the condensed water cylinder removed and read. The gross heating value of a gas when burned is obtained from the formula :—

$$H = \frac{WT}{G}$$

where H is the gross calorific value of 1 cubic foot of gas,
W is the quantity of water heated in litres,
T is the difference of temperature in degrees C. between the inflowing and outflowing water,
G is the quantity of gas burned during the experiment in cubic feet,

and represents the total heat generated by the combustion of the gas, including the latent heat of the steam produced, which steam is condensed to water in the calorimeter, giving up its latent heat of vaporisation to the circulating water. To obtain the net calorific value it is thus necessary to make the following correction :

The latent heat of steam is 538 calories, *i.e.* to evaporate 1 litre of water from the boiling point to steam would absorb as much heat without raising its temperature as would raise it 538° C., therefore in reducing steam to 1 litre of water at 100° C. 538 units would be liberated, and in bringing this down to atmospheric temperature (15° C.) a further 85 units should be added, making it in all 623 units per litre, or ·623 units per c.c. Therefore the number of c.c. of water condensed from 1 cubic foot of gas multiplied by ·623 will represent the heat generated during the burning of 1 cubic foot of gas due to the latent heat of the steam condensed. This should be deducted from the gross calorific value, the result being the net calorific value per ubic foot of gas in calories, which, multiplied by 3·97, gives it in B.Th.Us.

Example—

Temperature on inlet,	15·6° C.
,, ,, outlet,	26·8° C.
,, ,, outlet products,	15·6° C.
Gas passed,	0·10 cubic feet
Air temperature,	15·6° C.
Gas temperature,	15·6° C.
Water collected,	1·230 litres

$$\frac{1·230 \times 11·2}{·1} = 137·76 \text{ gross calories per cubic foot}$$

Water condensed, ... 1·8 c.c.

$1·8 \times 0·6 \times 10 = 10·8$ to be deducted from the gross

$137·76 - 10·8 = 126·96$ net calories per cubic foot

$126·96 \times 3·97 = 503·63$ B.Th.Us. (net) per cubic foot at N.T.P.

The "Boys" Calorimeter (fig. 40).—This calorimeter consists of three parts, which may be separated, or which, if in position, may be turned relatively to one another about their common axis. The parts are:—(1) The base carrying a pair of burners and a regulating tap. The upper surface of the base is covered with a bright metal plate held in position by three centring and lifting blocks, which are so placed as to carry. (2) The vessel, which is provided with a central copper chimney and a condensed water outlet. (3) Resting on the rim of the vessel is the water circulating system of the calorimeter attached to the lid.

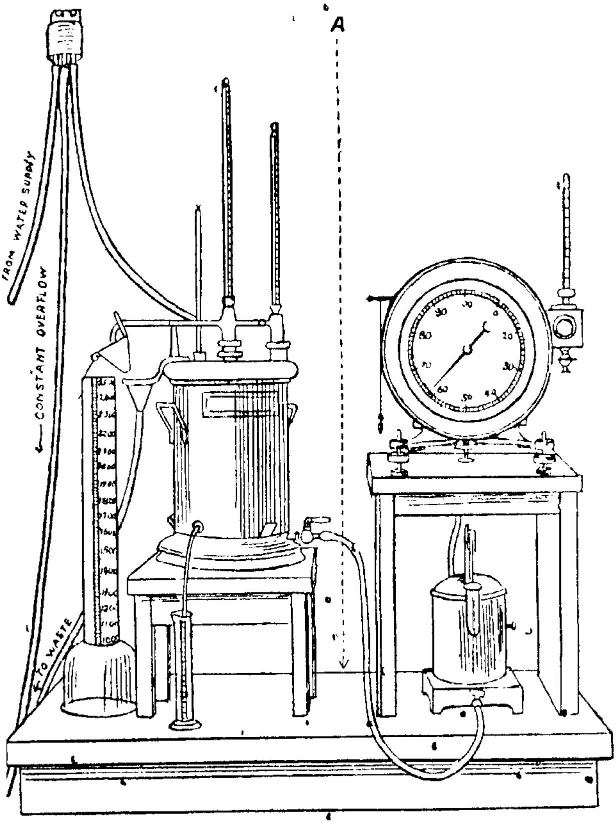

Fig. 40.

Except for the difference in design the action of the "Boys" calorimeter is the same as with the Junker instrument.

The Simmance-Abady Calorimeter.—In this instrument (fig. 41) the thermometers are placed side by side for convenience in reading, and there is also a water-level tube B provided, to enable the operator to see that there is a constant head of water, and therefore a constant flow of water through the calorimeter. The water flows three times from the bottom of the instrument to the top through narrow annular chambers, being conducted from the top of one annular chamber to the bottom of the succeeding one by four small tubes. Finally it flows past the outlet thermometer to the measuring cylinder or to waste. The tilting funnel C attached to the outlet enables the outlet water to be diverted as required without disturbing the rate of flow through the instrument. The gas burner is fitted with a mirror which enables the flame to be observed during a test. The calorimeter is packed with asbestos and lagged with mahogany strips to avoid radiation or absorption of heat.

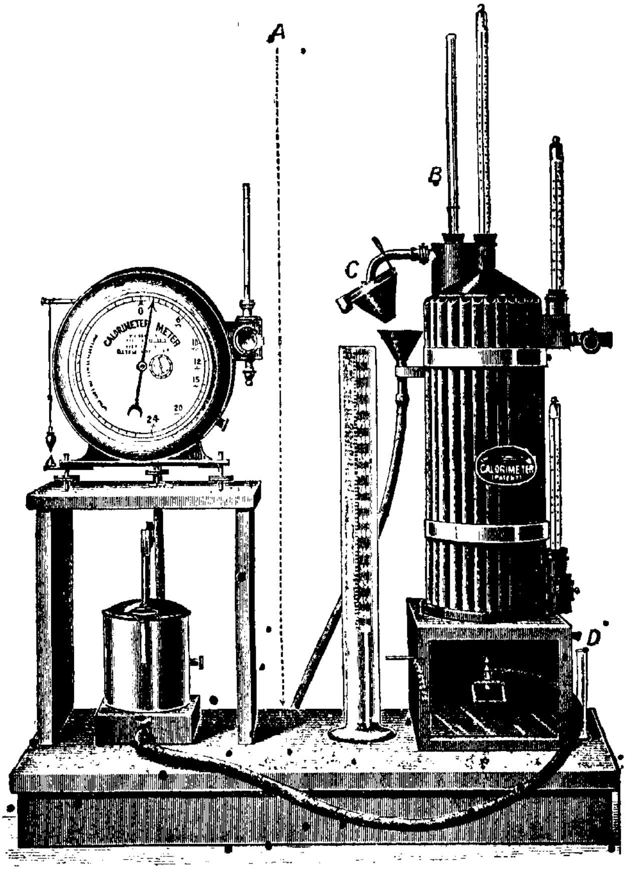

Fig. 41.

The condensed water, or condensed combustion products, are collected at D, when a net figure is required, the method of carrying out a test being exactly the same as with the Junker instrument.

Simmance-Abady's Recording Calorimeter (Calor Graph).—*Its principle.*—In this instrument an adjusted volume of gas is burned. The heat from this combustion is absorbed by a regulated quantity of air which then passes over one member of a differential thermometer, the other member of which is affected only by the room (air) temperature. The indication of the differential thermometer, which is thus a measure of the heat given off by gas on combustion, is recorded by means of a pen upon a chart passing over a clock drum.

The Constant Consumption of Gas.—The consumption of gas is automatically controlled by means of a balance governor, viz., by the difference in weights between equal volumes of air and the gas being tested, the valve closing in direct proportion to the gravity of the latter. When the densities of both air and gas change, the action is reversed, the extent of the action still being in exact ratio to the gravity (as distinguished from density).

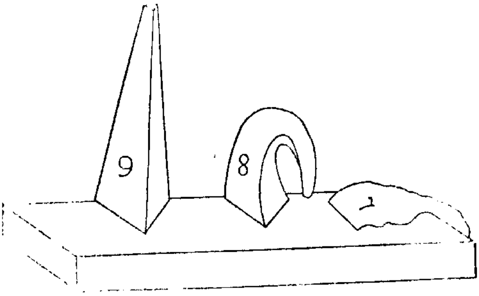

FIG. 42.

The Differential Thermometer.—The differential thermometer consists of two metal diaphragms filled with air, one at each end of a balance beam. Any movement of this beam is transferred to a pen which records upon the chart as it passes over a revolving drum driven by clockwork. The volume of air in the diaphragms will vary as their temperatures vary, so that they will expand or contract, and thus cause a movement of the beam, and a consequential movement of the pen. As, however, the right-hand diaphragm is affected only by the temperature of the room (cold air), while the left hand diaphragm is affected by the heat of the flame as well as the room temperature, the movement of the pen, which is the difference of the two effects, is proportioned to the heat obtained from the combustion of gas.

PYROMETRY.

The old-fashioned methods of using Seger cones (fig. 42) are not applicable to coke-oven practice.

The Thermo-Electric Pyrometer.—This type of pyrometer depends for its action on the fact that when a junction of two dissimilar metals is heated, an electro-motive force is set up at the junction which gives rise to an electric current when the circuit is closed. This electro-motive force varies with the temperature of the junction, hence the measurement of this electro-motive force may be made to measure also the temperature of the spot where the junction is situated. The metals used to form the junction are usually platinum and platinum alloys.

The Platinum Resistance Pyrometer (fig. 43).—This pyrometer works on the principle that platinum increases in resistance to a rise in temperature, therefore the measurement of the rise of the increase of resistance may be made to measure the temperature. The necessary current is obtained from two dry cells, it being measured by means of a galvanometer.

The Fery Radiation Pyrometer (fig. 44).—In this instrument the radiant energy from the source of heat is focussed by the aid of a mirror upon a small thermo-junction, which is therefore heated, and delivers current to the indicator, which is calibrated to read direct the temperature of the body at which the instrument is pointing. The advantages of these pyrometers are obvious, since the instrument need not be inserted into the furnace, and therefore does not undergo deterioration owing to the continuous action of the furnace gases as with the directly heated thermo-junction types.

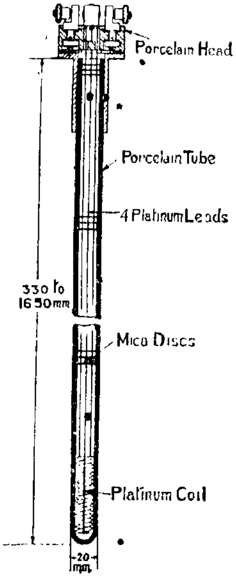

FIG. 43

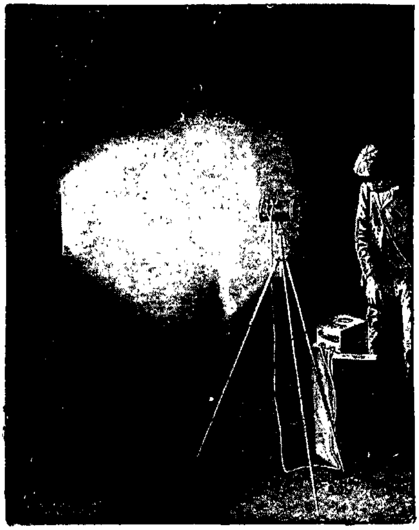

FIG. 44.

The Fery Spiral Pyrometer.—This instrument is a simpler and more compact, though less accurate, pattern than the Fery Radiation Pyrometer already described. The method of receiving the radiant heat and focussing it to form a heat image which covers a sensitive element in the telescope is exactly the same as for the Fery Radiation Pyrometer, but the difference consists in the sensitive element. Instead of using a thermo-couple which must be connected to a millivoltmeter outside the instrument, a very small bi-metallic spiral is used, and this controls the movement of a pointer which moves across a dial calibrated in temperature degrees. The instrument is thus entirely self-contained.

Fig. 45A shows the complete instrument on its tripod. Fig. 45B shows

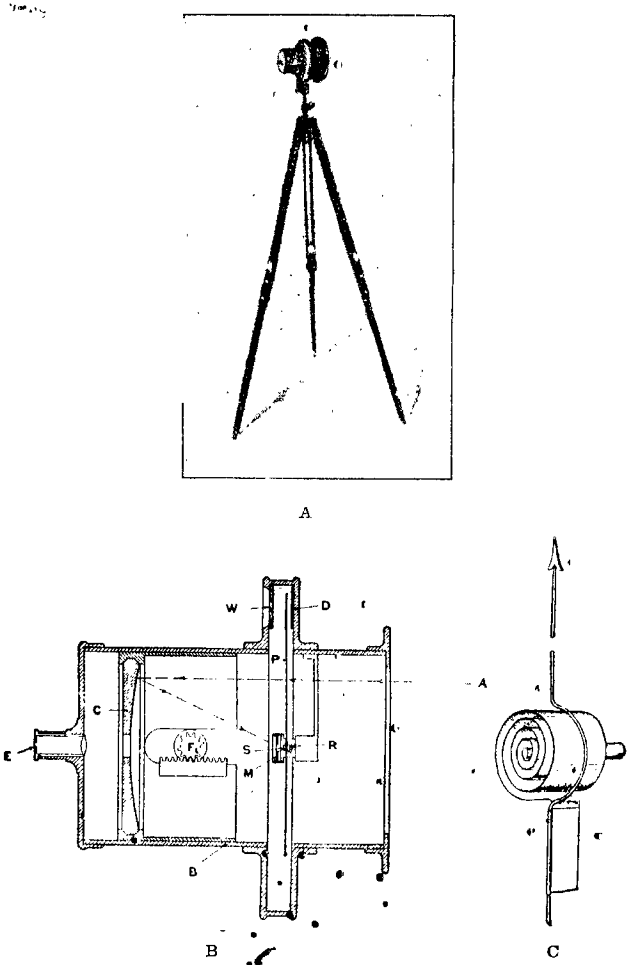

FIG. 45.

a sectional view through the pyrometer, R being the bi-metallic spiral, C the concave mirror, P the pointer, and D the scale. The spiral is shown, greatly enlarged, by Fig. 45C.

The action of the spiral when heated will be understood from the following consideration. If two strips of metal, having different coefficients of expansion with temperature, be soldered together to form one strip of double thickness, then, if the temperature be changed, one side of the strip will expand or contract at a different rate to the other. If the strip is fixed at one end only this varying expansion causes the free end to bend over so that it moves through a measurable space for a comparatively small change in temperature. In the Fery Spiral Pyrometer the strip built up of two dissimilar metals is rolled flat and very thin, and coiled into a spiral shape, so that as its temperature is raised the spiral uncoils. This spiral is very small, actually measuring less than $\frac{1}{8}$ of an inch (3 mm.) diameter, and $\frac{5}{64}$ths of an inch (2 mm.) wide. It is fixed at the centre and its free end carries a light

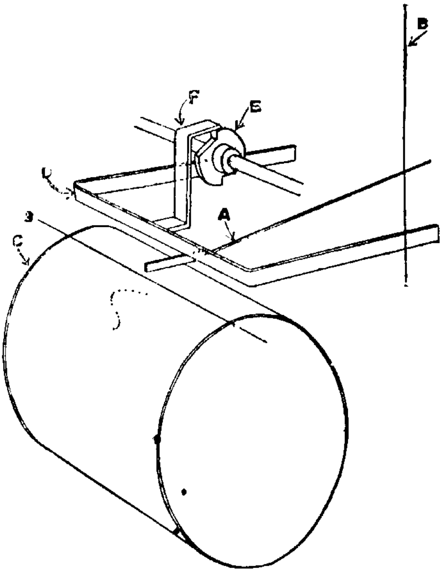

FIG. 46.

aluminium pointer which moves across a dial. The instrument is calibrated so that the reading of the pointer on the dial indicates directly the temperature of the body on which it is sighted.

The Cambridge Scientific Recording Galvanometer.—This recording galvanometer is so arranged as to give a series of records of the instantaneous deflections of a galvanometer pointer. The method employed for producing those records has the advantage of producing continuously visible records, while avoiding pen-friction. Fig. 46 is a diagram showing the essential parts of the recorder. A is a galvanometer pointer turning about its axis B, and overhanging a drum C. Between the pointer A and the drum C an inked thread G is stretched parallel to the axis of the drum, and at a short distance above its surface. A presser-bar D is situated above the galvanometer pointer, and this bar is normally held free of the pointer by means of a cam E and its follower F. At regular intervals the cam E makes a half-revolution, allowing the presser-bar D to fall upon the pointer A and then raising it again to its normal height. As the presser-bar falls, it depresses the pointer on to the drum, nipping the inked thread between the pointer and the paper. The pointer end has a knife-edge on its under side, which produces a dot upon the paper at the point of the intersection of the pointer and the thread, thus making a visible record of the instantaneous deflection of the galvanometer.

The galvanometer pointer is hinged so that it can be depressed without bending the suspension. In the intervals between the reproduction of the dots the galvanometer is, of course, free to take up its true deflection without frictional errors. As the dot is always produced where the thread and the pointer intersect, it will be obvious that by suitable arrangements of the galvanometer coefficient, paper with rectangular co-ordinates of uniform scale can be used.

CHAPTER IX.

BENZOL RECOVERY PLANT.

Benzol in Benzolised and Debenzolised Oils.—250 c.c. of the benzolised or 500 c.c. of the debenzolised oil is distilled from a litre distilling flask up to 200° C. The distillate (a mixture of light oil and water) is separated, and the oil distilled from a 100 c.c. round-bottom flask, fitted with a two-bulb fractionation column.

The fractions (1) up to 120° C., (2) 120° C. to 160° C., and (3) 160° C. to 180° C. are collected separately.

The total distillate at 180° C. gives the percentage of crude benzol in the oil, the three fractions being collected separately, in order to be able to form an idea of the quality of the benzol.

Total Sulphur in Benzol, Toluol, etc.—(*a*.) The following method[1] has been tried by the author and found to give very satisfactory results. The benzol or toluol is weighed into a tared flask (fig. 47), and evaporated by drawing air through it, the benzolised air passing through the silica tube heated to redness at two points, to ensure complete combustion. The products of combustion are passed through a solution of pure sodium hydrate, contained in wash bottles. A little bromine or hydrogen peroxide is added to facilitate oxidation, the solution acidified with hydrochloric acid and filtered, the sulphur being precipitated as barium sulphate.

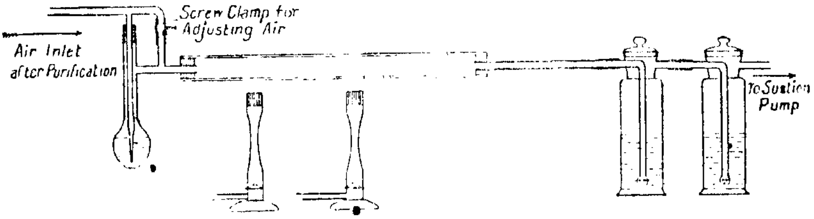

FIG. 47.

(*b*.) Hewett's modification of the Roland Wild fuel calorimeter (fig. 48) can be used successfully for this estimation. The body of the crucible is of nickel, to which the thread is firmly soldered. The lid is turned to a loose fit, to allow of easy removal, the tightness of the joint depending upon the smooth surfaces and the paper washer. The crucible lid forms one pole and the pillar the other; the latter being insulated by a mica washer and a small rubber sheath between the nuts.

The estimation is carried out as follows:—20 grams of sodium peroxide is separately weighed out. The crucible is then tared and less than 1 gram of the material weighed in, preferably from a small dropping tube. The sodium peroxide is then added, and the whole quickly and thoroughly mixed, using for this purpose a piece of bent nickel wire. After tightly closing the crucible, the mixture is fired by passing a current from a suitable accumulator, and if necessary the crucible prevented from becoming red hot by immersion in distilled water. The crucible is then opened, and the contents thoroughly washed into a beaker, or, better still, the crucible itself is immersed. Rapid solution of the fused mass takes place. The crucible and lid are well washed, the washings being added to the contents of the beaker, which are made slightly acid with hydrochloric acid, this acid solution being filtered, boiled, and the sulphur precipitated with barium chloride in the usual manner.

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[1] *Gas World*, Jan 1917.

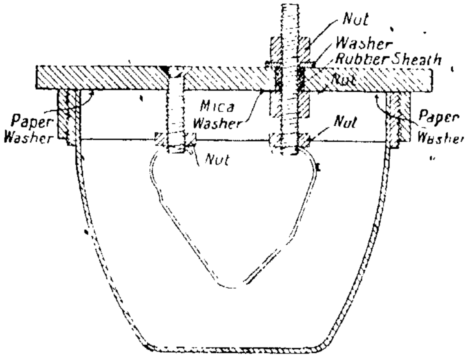

FIG. 48.

(c.) Another method.[1]—A convenient quantity (0·7 – 1·5 grams) of the substance is weighed into a small platinum crucible containing 3 to 4 grams of a mixture of four parts of pure lime to one of anhydrous sodium carbonate, and intimately mixed with it. The crucible is then filled with the mixture, covered with a small platinum dish, and inverted as shown (fig. 49), the dish being then also filled with the mixture. A thick pad of asbestos is placed over the crucible, and the whole placed into a muffle furnace and kept at a bright red heat for two hours. The asbestos is used to keep the

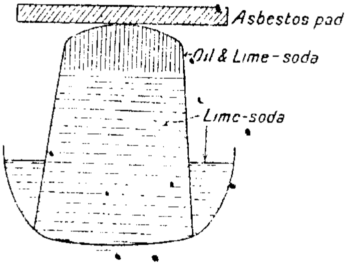

FIG. 49.

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[1] *J.S.C.I.*, 15th December 1905.

top of the crucible cool until the oxidising mixture is hot, when it is removed, and the oils distil downwards, the sulphur compounds being oxidised and arrested. After cooling, the mixture is washed into water, the sulphides oxidised with bromine and the solution then filtered, boiled, and the sulphur precipitated with barium chloride.

Note.—With volatile liquids, the weighings should be carried out as quickly as possible, care being also taken to handle the base of the crucible as little as possible.

(*d*) The following method is also recommended:—Fit up the apparatus as shown (fig. 50), place in the lamp 80 c.c. methylated spirits and 20 c.c. of the sample. Place round the lamp lumps of sesquicarbonate of ammonia. Cover the exit of B and the inlet C with distilled water, and start the suction. When all is burnt, add to the lamp another 20 c.c. of methylated spirit and burn again until empty. Add the water from A and B together, and treat as with the condensings obtained in the referee's gas test. Also test the liquid in C, which should be free from sulphur.

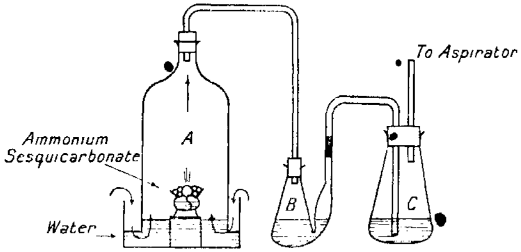

FIG. 50.

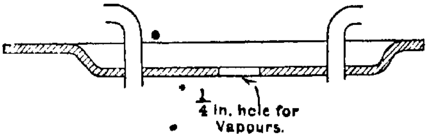

FIG. 51.

(*e*) The following method, by the author,[1] is useful for heavier oils such as naphthas, etc.:—0·25 gram of the oil is weighed on to 2 grams of precipitated silica and intimately mixed with it 5 grams of sodium peroxide, and 0·25 gram of potassium chlorate are then weighed out and mixed with the silica and oil in a nickel crucible of about 40 c.c. capacity, and which is fitted with a lid into which three holes have been drilled as shown (fig. 51). Into the two side holes fine glass tubes are fixed with which to insulate the wires connecting a resistance wire fitted inside as shown (fig. 52). The crucible is placed in a dish of distilled water, the level of the water being ½ inch below the lid. A basin is inverted over the central hole to prevent any of the mixture being lost by splitting. The combustion is then started, and only requires a few seconds, after which the crucible is overturned into the water, and the whole boiled up. The solution is then filtered, acidified, and the sulphur precipitated as before.

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[1] *Gas World*, 20th January 1917.

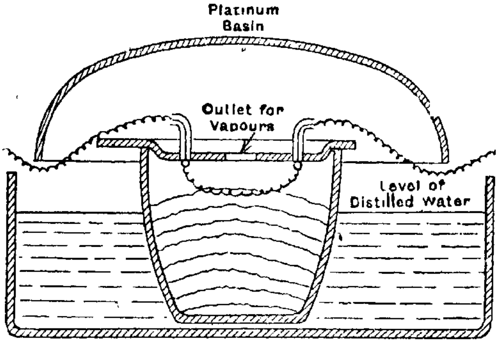

FIG. 52.

The Flash-point of Spirits and Oils.—Oils sent by rail are classed under three heads, according to their flash-point, for which different rates are charged.

The flash-point of a spirit or oil is the empirical temperature at which it gives off sufficient vapour to ignite momentarily on the introduction of a flame or spark, when the oil is heated at a given rate, in an apparatus of given construction and dimensions, and a defined igniting agent is applied in a given manner.

The legally recognised method of determining the flash-point of an oil in the United Kingdom is that designed by Sir Frederick Abel and embodied in the Petroleum Act of 1879.

The manipulation of the Abel Tester (fig. 53) is there set forth as follows:—

"PETROLEUM ACT, 1879 (42 and 43 Vict. C. 47).

"*Mode of testing Petroleum so as to ascertain the temperatures at which it will give off inflammable vapour.*

"The test apparatus should be placed for use in a position where it is not exposed to currents of air or draughts.

"The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel.

"The temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing hot or cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

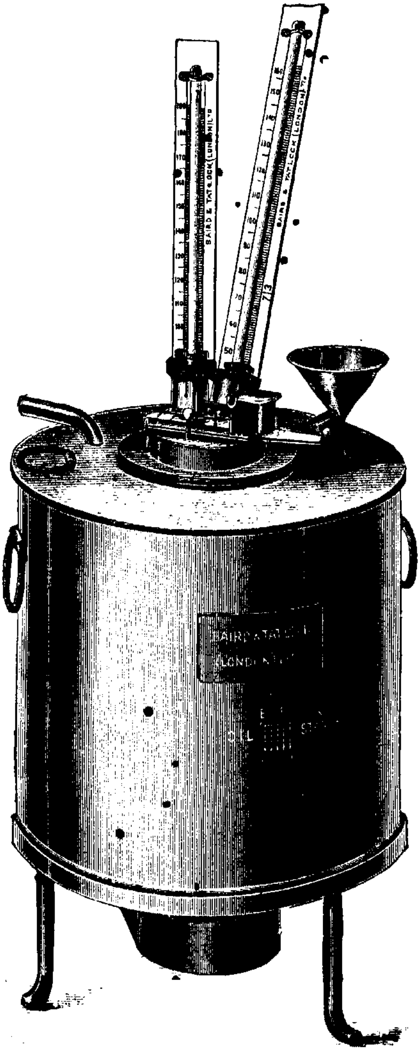

Fig. 53.

"If the water has been heated too highly, it is easily reduced by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

"When a test has been completed, this water-bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus and the next is proceeded with.

"The test-lamp is prepared for use by fitting it with a piece of flat-plaited candle-wick, and filling it up with colza or rape oil up to the lower edge of the opening of the spout or wick table.

"The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter; and this size of flame, which is represented by the projecting white lead on the cover of the oil-cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

"When gas is available it may be conveniently used in place of the little oil-lamp, and for this purpose a test-flame arrangement for use with gas has been devised, which may be substituted for the lamp.

"The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup.

"In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° F. the samples to be tested should be cooled down (to about 60° F.) by immersing the bottles containing them in cold water, or by any other convenient method.

"The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered.

"When the cup has been placed in a proper position, the scale of the thermometer faces the operator.

"The test-lamp is then placed in position upon the lid of the cup; the lead line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion and the rise of the thermometer in the petroleum cup is watched.

"When the temperature has reached about 66° F. the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree in the following manner:—

"The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation.

Note.—If it is desired to employ the test apparatus to determine the flashing point of the oils of very low volatility, the mode of proceeding is to be modified as follows:—

"The air chamber which surrounds the cup is filled with cold water to a depth of 1½ inches and the heating vessel or water bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus and kept there during the entire operation. If a heavy oil is being dealt with, the operation may be commenced with water previously heated to 120° instead of with cold water."

ANALYSIS OF CRUDE BENZOL

Recovered either from Gas by Scrubbing or from Tar by Distillation.

(According to Colman and Yeoman, in a paper before the London Section of the Society of Chemical Industry.)[1]

Preliminary Distillation.—500 c.c. of the sample is directly distilled, using a Young 12-bulb pear column, and the distillate to 200° C. collected.

PURIFICATION OF THE DISTILLATE TO 200° C.

In order to purify the distillate, not less than 200 c.c., and preferably at least 250 c.c., is shaken with one-quarter of its volume of 10 per cent. aqueous caustic soda, allowed to settle, the caustic layer run off, and the oil washed with water, which is also run off, and the volume of residual oil measured. The loss of volume represents approximately the volume of tar-acids in the volume of oil taken.

After alkali washing, the remaining oil is shaken for 5 minutes with 8 per cent. of its volume of concentrated sulphuric acid and allowed to settle for 15 minutes.

In the process of shaking with concentrated sulphuric acid, small quantities of aromatic hydrocarbons are absorbed in addition to olefines, so that the percentages of the former subsequently found are always rather lower than the quantity present in the original material. As, however, in practice, the products have also always to be washed with concentrated sulphuric acid, the results obtained for the percentages of aromatic hydrocarbons truly represent the maximum quantities of these which could be obtained, provided that the washing to which they are subjected on the small scale is not more severe than that which they receive in large scale practice to remove the unsaturated compounds. The quantity of acid given above, namely, 8 per cent. of 95 per cent. acid with 5 minutes' shaking, has been found to effect a satisfactory removal of the unsaturated compounds with all samples tried, and not to cause extensive absorption of aromatic hydrocarbons, and such absorption of these as does take place chiefly affects the xylenes, which are more readily attacked by sulphuric acid than is toluene, whilst benzene is still less affected.

Satisfactory washing can be obtained with many samples by the use of less than 8 per cent. of sulphuric acid, but it is not an easy matter to judge, except by trial, how far this can be reduced, and the use of the full 8 per cent. does not appear to cause undue removal of the benzene, and toluene in any case, if shaking is not prolonged for more than the specified 5 minutes.

The strength of acid used should closely approximate to 95 per cent. H_2SO_4. Water is then carefully added down the side of the separating funnel, so that it floats on the top of the acid layer, which thus becomes visible. With some oils the darkening on shaking with acid is so great that the boundary between the two layers can only be perceived with great difficulty until water is added in this manner. The acid layer is then run off, and the oil washed by allowing a thin stream of water to fall through it without shaking. After running off the water, the oil is shaken successively with 10 per cent. aqueous caustic soda, and finally with water, only gentle shaking being employed, so as to avoid, as far as possible, the formation of emulsions.

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[1] *J.S.C.I.*, 31st March 1919.

The difference between the volume now remaining after complete separation of water and the volume remaining after washing with alkali gives an approximate indication of the volume of unsaturated hydrocarbons (chiefly olefines) which have been absorbed by the sulphuric acid.

In addition to the olefines, other unsaturated hydrocarbons are present (dienes, etc.) which are not absorbed by the sulphuric acid, but in its presence chiefly undergo polymerisation, yielding high-boiling hydrocarbons of unknown constitution, boiling mainly from 300° to 400° C., which remain dissolved in the oil, the olefines also yielding polymerised hydrocarbons to some extent. The actual amount of such condensable hydrocarbons varies greatly, and is much higher in products derived from the carbonisation of petroleum products than in those obtained from coal. An approximate estimation of the quantity of these is obtained from the volume of the residue left at 200° on refractionating the washed oil.

This oil, after freeing from water as completely as possible, is again distilled from a round-bottomed flask fitted with a Young 12-bulb pear column, at the rate of 4 c.c. per minute, and separated into fractions. The method of collecting the fractions is varied somewhat according to the composition of the washed oil.

(1) Where not less than 50 per cent. of the washed oil distils under these conditions below 90° C., the fractions are directly collected as follows:—

(*a*) Up to 90°, this fraction then containing only benzene and toluene, together with carbon bisulphide, and paraffins of similar boiling point.

(*b*) 90°–140°, this fraction consisting of benzene, toluene, and xylene, except for paraffins of similar boiling point.

(*c*) 140°–160°, consisting of xylenes, cumenes, etc., with paraffins.

(*d*) 160°–200°, consisting of higher homologues of benzene, with some paraffins.

(*e*) Residue at 200°, consisting chiefly of the polymerised hydrocarbons formed by the action of sulphuric acid on the dienes, etc., in the original oil.

(2) If the amount boiling below 90° is less than 50 per cent., as is often the case with crude naphtha from coal-tar, some xylene may also distil over with benzene and toluene below 90°. Where the distillate up to 90° does not amount to 50 per cent. therefore, the first fraction is collected up to 95°, and the second fraction from 95° to 140°, and the remainder of the fractionation made as in (1). The fraction up to 95° is then refractionated, and the distillate up to 90° collected. The residue at 90° contains all the xylene and is then added to the fraction 95°–140°, the combined amounts forming the fraction 90°–140°.

(3) When the proportion of xylene and higher-boiling constituents is low, it is often not possible to continue the distillation up to 140°, owing to vapours in the later stage all condensing in the fractionating column. In such cases, xylene is added to the residue after the fraction up to 90° has been collected, and the distillation then continued to 140°. In that case the determination of the fractions 140°–160° and 160°–200°, and residue at 200° is omitted, or, if required, a larger quantity of the original oil must be taken. The xylene must not be added before the fraction up to 90° is collected, as otherwise xylene would come over with that fraction and would count in the analysis as toluene.

Sometimes the oil after washing with sulphuric acid, caustic soda, and then with water, forms a very persistent emulsion with the latter, which is only separated with great difficulty. In such cases, the emulsion may be steam distilled, when the polymerised unsaturated hydrocarbons remain behind, the distillation being continued until the volume of condensed water approximately equals half the volume of spirit condensed. The difference between the volume of the steam distillate obtained after separation of water and volume of oil after acid washing gives an approximate figure of the total unsaturated hydrocarbons present, *i.e.* the combined amount of olefines and polymerised hydrocarbons. In the subsequent fractionation of the steam distilled oil this is stopped at 160°, and the residue at 160° taken as the fraction 160°–200°. Some loss of the lower-boiling constituents, especially of benzene, is, however, difficult to avoid when steam distillation is carried out.

Determination of Benzene, Toluene, and Xylene in the Fractions "up to 90°" "90°–140°," and in Commercial Benzol and Commercial Toluol.

Before these methods can be adopted it is necessary that the samples shall be freed as completely as possible from unsaturated hydrocarbons and phenols. This is the case when the fractions have been properly washed with sulphuric acid and caustic soda as described, but in the case of commercial benzol and toluol this may not be the case.

The ordinary method of ascertaining whether such products are sufficiently free from unsaturated hydrocarbons consists in shaking 90 c.c. of the sample with 10 c.c. of sulphuric acid of 90 per cent strength, and judging from the coloration of the acid layer whether these have been sufficiently washed, this not being the case if the coloration exceeds a deep yellow or light brown colour. This test, although useful as a quick test for works control purposes, is far from satisfactory as a reasonably accurate method for giving a comparative indication of the amount of unsaturated compounds present, and is by no means certain in its indications—some samples which are in reality well washed giving a bad discoloration, whilst others, in reality badly washed, may only give a slight discoloration. A much more satisfactory test, which is quickly carried out and gives a relative quantitative indication of the proportion of unsaturated hydrocarbons present, is the determination of the quantity of oxygen the sample will absorb from an acid solution of potassium permanganate, at the ordinary temperature. This test is carried out as follows :—

80 c.c. of water and 10 c.c. of dilute sulphuric acid (made by adding 1 part by weight of concentrated sulphuric acid to 3 parts by weight of water) are placed in a stoppered bottle of about 300 c.c. capacity, 10 c.c. of the commercial spirit to be examined added, and the whole shaken. The temperature of the liquid should be between 15° and 20° C. 50 c.c. of N/10 potassium permanganate is then added, and the whole shaken continuously for exactly 3 minutes ; if at the end of the first half minute the permanganate solution is markedly decolorised, a further 50 c.c. of N/10 permanganate is added, and the shaking then continued for a further 2½ minutes. The excess of permanganate is then destroyed by the addition of 10 c.c. of a 10 per cent. potassium iodide solution, with vigorous shaking. The resulting solution containing iodide is then titrated with N/10 sodium thiosulphate solution, shaking well between each addition, until both layers in the bottle become colourless. The end-point of the titration is sharply indicated by the final

disappearance of the violet colour from the spirit layer, and there is no need to add starch as indicator unless the original spirit was coloured. The number of c.c. of thiosulphate solution required for the titration is deducted from the volume of permanganate solution taken, the difference giving the number of c.c. of decinormal permanganate solution reduced by 10 c.c. of the sample under the above conditions, and this figure gives a comparative indication of the extent to which the sample contains oxidisable impurities. If the number of c.c. of permanganate solution reduced by 10 c.c. of the sample is multiplied by 0·008 (1 c.c. N/10 $KMnO_4$ = 0·0008 gram oxygen) the resulting figure gives the number of grams of oxygen absorbed from permanganate by 100 c.c. of the spirit.

Well-washed samples show the reduction of from 1 to 10 c.c. of permanganate for 10 c.c., or 0·008 to 0·08 gram oxygen absorbed per 100 c.c., but others give much higher figures owing to insufficient washing.

A completely unwashed spirit may also be tested in a similar manner to ascertain approximately the amount of washing it requires. In such cases, 10 c.c. of the sample is diluted with pure, well-washed, benzene to 100 c.c., and 10 c.c. of the diluted spirit taken for the test.

Any insufficiently washed commercial benzol or toluol, *i.e.* any sample giving a higher oxygen absorption than 0·2 gram per 100 c.c. should be subjected to further acid-washing before testing. For this purpose a volume of 150–250 c.c. of the sample is shaken with 2 per cent. of 95 per cent. sulphuric acid, if the oxygen absorption is about 0·2 gram per 100 c.c. an additional 1 per cent. of sulphuric acid being used for each additional 0·1 gram of oxygen absorption. After removal of the acid layer and washing with water, aqueous caustic soda, and again with water as previously described, the washed spirit is transferred to a round-bottomed flask, fitted with a glass tube for the introduction of steam and connected to a condenser, and distilled without introduction of steam until about two-thirds has distilled over; steam is then carefully blown through the liquid until about 50 c.c. of water has condensed for each 100 c.c. of the sample taken. The difference between the volume of spirit in the distillate and the volume originally taken gives the loss due to acid washing, the percentage of which is calculated and allowed for in determining the percentages of aromatic hydrocarbons in the original insufficiently washed sample.

Analysis of Fractions "up to 90°" and "90°–140°."

The percentage of benzene and toluene in the fraction up to 90°, and of benzene, toluene, and xylene in the fraction 90°–140°, may be determined with considerable accuracy by distilling these under specified conditions from a simple distillation flask of standard dimensions, and a comparison of the volume of the fractions obtained between fixed temperature limits with those obtained by distilling mixtures of known volumes of the pure hydrocarbons in the same apparatus and under the same conditions.

The apparatus required for the purpose consists of (1) A standard Engler 100 c.c. distillation flask, as employed in the petroleum industry, having the following dimensions: internal diameter of bulb, 6·5 cm.; length of neck, 15·0 cms.; internal diameter of neck, 1·6 cms.; vertical height of side tube above surface of liquid when flask is charged with 100 c.c., 9·0 cms.; angle of side tube, 75·0°. Flasks which do not vary more than 3 per cent. from any of these dimensions may be employed.

(2) An efficient water-cooled condenser.—This is preferably a 10-inch Liebig condenser placed vertically, the connection with the flask being made by an adapter or by having the side tube of the flask sufficiently long, and bending it to fit the upper end of the condenser. The condenser used must in any case be of a form which drains quickly and as completely as possible.

(3) A set of calibrated graduated cylinders (50 and 100 c.c.).

(4) An accurate thermometer, which is fixed in the distillation flask with the top of the bulb just below the bottom of the side tube. With the above dimensions of the flask, the length of stem below the cork is then about 100 mm.

The accuracy of the determinations probably depends more on the correct reading of the thermometer than on any other single point. The thermometer used should preferably have a bulb of moderate size, and should be graduated in ⅕° C. over a range of at least 70° to 130°; the 80° graduation mark should be about 140 mm. from the bottom of the bulb, so that when the thermometer is fixed in the flask in the correct position this point is well above the top of the cork.

Calibration of the Thermometer.—The thermometer should be graduated with an immersion of 100 mm. (this being the extent to which the stem is heated by the vapours under the conditions of the test), and then no correction is necessary for the length of the mercury column not heated by the vapour. Previous to use, it should be verified, or the corrections ascertained, for the temperatures 80°, 85°, 90°, 100°, 105°, and 116°, with 100 mm. immersion. In order to avoid mistakes in reading the thermometer it is convenient to put a distinctive mark on it at the actual graduation found to correspond on that thermometer to the corrected temperatures 80°, 85°, 90°, 100°, 105°, and 116°, Nat. Phs. Lab. standard.

Correction for Barometer.—Before making a test the reading of the barometer in millimetres (corrected to 0° C.) is taken, and the barometer correction ascertained from the usual formula—barom. corrn. = 0·00012 (760-p) (273 + t°), where p the height of the barometer in mm. corrected to 0° C. and t° the boiling point. The magnitude of the correction increases with increasing boiling point, but within the range of 80° to 120° the following table of corrections for barometric pressures from 772 to 720 mm. is of sufficient accuracy:—

P.	Corr.	P.	Corr.	P.	Corr.
772	− 0·55	754	+ 0·30	736	+ 1·10
770	− 0·45	752	+ 0·35	734	+ 1·15
768	− 0·35	750	+ 0·45	732	+ 1·25
766	− 0·30	748	+ 0·55	730	+ 1·35
764	− 0·20	746	+ 0·65	728	+ 1·45
762	− 0·10	744	+ 0·75	726	+ 1·50
760	0·00	742	+ 0·85	724	+ 1·60
758	+ 0·10	740	+ 0·90	722	+ 1·70
756	+ 0·20	738	+ 1·00	720	+ 1·80

A thermometer which has been calibrated with the stem completely immersed may also be used for the test, but in that case the correction for unheated mercury column must be made in addition to the barometer correction, in accordance with the usual formula: stem correction = 0·000143 (T−t°)N, where T = the observed boiling point, t° the temperature of the air around the unheated portion of the stem, and N the length of the emergent mercury column, expressed in scale degrees.[1]

Before using a thermometer for the test, a few blank tests should be made with it, using mixtures made up of known amounts of pure benzene and toluene, and of pure benzene, toluene, and xylene, in order to ascertain that the results obtained with the thermometer are substantially correct. It has been found in one or two cases that certain thermometers although quite correctly graduated, do not give correct results, as they have a pronounced lag. The cause of this has not been definitely ascertained, but appears to be due to the nature of the glass used in the manufacture of the thermometer. It is also advisable to carry out periodically similar blank tests on known mixtures with any thermometer in use for the analysis, to make sure that the readings given have not undergone change since its verification.

Method of Distillation.—In carrying on the distillation, a measured volume of the liquid to be tested is distilled from the Engler flask at the rate of about 7 c.c. per minute. A slightly higher rate has no material effect on the results, but if the rate falls much below 7 c.c. appreciably increased fractional condensation takes place in the top and neck of the distilling flask, and may cause incorrect results. The flask is heated by means of a small bunsen flame impinging directly on the bottom of the flask, the distillation being carried out at a spot as free from draught as practicable, a cylinder of fine wire gauze being also placed to surround the burner and flask up to the level of the top of the bulb of the flask. The distillates are collected in the graduated cylinders, and when the thermometer reaches the specified temperature, the flame is extinguished, the condenser allowed to drain, and the volume of the distillate measured.

MEASUREMENT OF VOLUMES AND DETERMINATION OF SPECIFIC GRAVITY.

The specific gravities employed in the determinations are, throughout, those of the liquids at 15·5° C. compared with water at 15·5° C., and all volumes given are those of the liquids at 15·5° C. To correct the observed specific gravity at any other temperature to that 15·5°, in the case of spirits, 0·0009 is added for each 1° C. the observed temperature is above 15·5°, or deducted for each 1° C. below that temperature. In the case of tar or products consisting chiefly of high-boiling oils, the factor used is 0·0007.

Fraction "up to 90°" and Commercial Benzol.—When mixtures of benzene and toluene are distilled from a distillation flask under the specified conditions, the percentage of distillate at any given temperature is constant, and if the volume of distillate from 100 c.c. of the mixture to any temperature is determined for a definite rate and for a definite size of fractionating flask, then with an unknown mixture of benzene and toluene the percentages of benzene and toluene can be found by comparing the volume of distillate obtained under the same conditions with that found in the case of mixtures containing known amounts of the two constituents.[2]

The results obtained with pure mixtures of benzene and toluene are most conveniently plotted out in the form of a graph, temperatures suitable for the collection of the distillate being 85° corr. for mixtures containing up to 25 per cent. of toluene, and 90° corr. for mixtures containing from 20 to 40 per cent. of toluene. The percentages of toluene are plotted as ordinates, and the percentages of distillate as abscissæ. In compiling Graph I the following mixtures were employed:—

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[1] Tables for the value of this correction are given in Young's *Fractional Distillation* (Macmillan & Co.), p. 13, and a graph for the purpose by Wheeler (*J.S.C.I.*, 1916, 1198).

[2] James, *J.S.C.I.*, 1916, 236.

Up to 85° corr.		Up to 90° corr.	
Benzene. c.c.	Toluene. c.c.	Benzene. c.c.	Toluene. c.c.
97	3	80	20
94	6	75	25
90	10	70	30
85	15	65	35
80	20	60	40
75	25	55	45

In the case of the fraction "up to 90°" or of any mixtures of benzene and toluene only, not containing more than 45 per cent. of the latter, 100 c.c. (or less if the quantity available is insufficient) is distilled from the Engler flask under the same conditions, and the percentage of distillate to 85° corr. or 90° corr. ascertained. From Graph I the percentage of toluene is read off corresponding to the percentage of distillate found, that of benzene being found by difference.

Carbon Bisulphide and Paraffins.—When these impurities are absent, the reading obtained from the graph gives directly the percentages of benzene and toluene in the sample. The percentages of the above impurities, when present, can be ascertained, together with the necessary correction in the amounts of benzene and toluene, from a determination of the specific gravity of the fraction or sample before and after removal of carbon bisulphide from it.

Carbon bisulphide.—To carry out this determination, the specific gravity of the sample is taken by any method giving results accurate to the third place of decimals. A further 100 c.c. (or the combined distillate to 85° or 90° and the residue from the distillation test) is then mixed with 100 c.c. of alcohol or industrial methylated spirit (free from paraffins), 5 grams of roughly powdered caustic soda added, and the whole shaken for five minutes. 200 c.c. of water is then added, with renewed shaking; after settling, the lower aqueous layer is run off, and the spirit washed twice with successive quantities of 25 c.c. of water and dried with ignited calcium chloride. The specific gravity of the dried spirit is then taken accurately to the third decimal place.

From the specific gravity of the spirit, before and after removal of carbon bisulphide, the percentage of carbon bisulphide present may be calculated,[1] on the assumption that the specific gravity of carbon bisulphide is 1·27, and that no expansion or contraction occurs on mixing the latter with benzene or mixtures of benzene and toluene, for then if a is specific gravity of spirit after removal, and b the specific gravity before removal of CS_2, and x the percentage by volume of CS_2,

$$1{\cdot}27x + (100 - x)\,a = 100b, \text{ or } x = 100 \times (b - a) \div (1{\cdot}27 - a).$$

In fact, however, the assumption that no expansion or contraction occurs on mixing carbon bisulphide with benzene or mixtures of benzene and toluene is incorrect, as appreciable expansion does occur,[1] and the observed specific gravity of mixtures of benzene or of benzene + toluene with carbon bisulphide in known proportions, is always lower than that calculated from the percentage of the components and their specific gravity by a definite amount, k, and to obtain the percentage of carbon bisulphide by volume corrected for this expansion, the value, $b + k$, must be substituted for b in the above formula, which then becomes

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[1] See Nickels, Allen's *Comm. Org. Analysis*, vol. ii., part 2, p. 183; Spielmann, *J.S C.I*, 1916, 396.

$$x = 100 \times \{(b + k) - a\} \div (1 \cdot 27 - a).$$

The value of k varies with different proportions of carbon bisulphide and also slightly with differences in the proportion of toluene present, but an average figure for this value for percentages of carbon bisulphide up to 5 per cent. may be taken without material error as follows:—

Per cent. CS_2.	k.
1	0·0010
2	0·0015
3	0·0020
4	0·0024
5	0·0027

Graph 2 has been compiled to enable the direct reading off of the percentage of CS_2 in the sample from the specific gravity before and after removal of CS_2, the correction for expansion being made in setting out the graph. The lower line of ordinates gives the observed specific gravity before CS_2 removal, and the abscissæ the observed specific gravity after CS_2 removal, the percentage of CS_2 being read off from those on the broken black lines marked 0–5 per cent. of CS_2.

Paraffins.—In a similar manner the percentage of paraffins present may be calculated from the observed specific gravity of the sample after removal of CS_2, and the specific gravity which a sample containing the percentage of toluene found would have if paraffins were absent. As no material expansion occurs on mixing benzene and toluene at any rate with the amounts of the latter found in the fraction "up to 90°," or in commercial benzol, this last figure may be directly calculated with sufficient accuracy from the percentage of benzene and toluene found by the distillation to 85° or 90°.

Expansion does, however, occur on mixing paraffins with benzene or mixtures of benzene and toluene, and correction must be made on this account in the case of paraffins as well as with CS_2, and the necessary formula becomes.—percentage by volume of paraffins in CS_2-free spirit

$$= 100 \times \{(a + k^1) - c\} \div (p - c)$$

where a is observed specific gravity after CS_2 removal, c the specific gravity of paraffin-free benzene-toluene mixture calculated from the distillation to 85°, p the specific gravity of paraffins, and k^1 the correction for expansion.

The exact specific gravity of the paraffins present is unknown, but it has been found by isolation of them from these products, that this may be taken without material error as 0·730 in this fraction up to 90°, or in commercial benzol. The value of k^1 also varies considerably according to the percentage of paraffins present (the expansion being much greater on the addition of the first 1 per cent. than for any succeeding 1 per cent.), and also slightly with the percentage of toluene in the mixture, but for practical purposes the following values of k^1 may be taken :—

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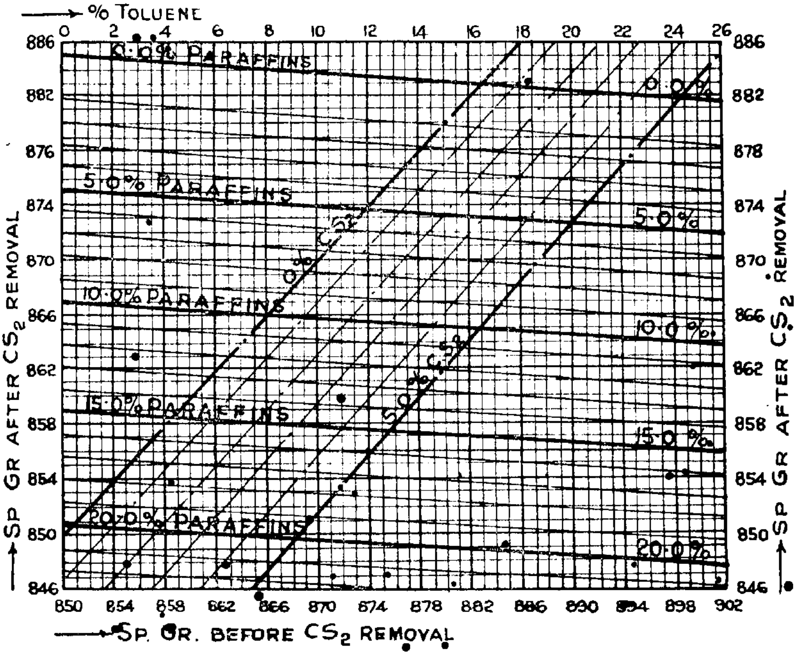
[1] See F. D. Brown, *J. Chem. Soc.*, 1879, 35, 552; 1881, 39, 205.

Paraffins per cent.	k^1
1	0·0017
5	0·0021
10	0·0025
15	0·0029
20	0·0033

From the observed specific gravity of the sample after removal of CS_2 and the percentage of toluene found by Graph 1 uncorrected for paraffins, the percentage of paraffins in the sample after removal of CS_2 may be read directly from Graph 2. The upper line of ordinates gives the "uncorrected" percentage of toluene found, and the abscissæ the observed specific gravity of the sample freed from CS_2, the percentage of paraffins being read off from these on the full black lines marked 0–25 per cent. of paraffins.



GRAPH 2.—Percentage of CS_2 and Paraffins in Fraction "up to 90°" and in Comm. Benzol.

The percentage of paraffins thus found is that in the sample after removal of CS_2, and to obtain the true percentage of the paraffins in the original sample this figure must be multiplied by 100 − C, and divided by 100 where C is the percentage of CS_2 found in the sample.

The percentages of benzene and toluene found by Graph 1 are those which would be the case if no carbon bisulphide and paraffin were present. The total number of volumes of benzene + toluene present in 100 volumes is 100–C–P, where C and P are the percentages found of these two impurities. In the distillation to 85° or 90° carbon bisulphide behaves as though it were benzene, and if paraffins are absent but CS_2 present, the result obtained by Graph 1 gives the true percentage of toluene correctly, and the true benzene figure is 100–C–T where T is the percentage of toluene found.

Whether the paraffins, when present, are of such boiling point that they are proportionately divided between the benzene and toluene fractions is uncertain and probably variable with different samples, but the evidence appears to show that they are in fact roughly proportional, and that if this is assumed no material error results.

Making this assumption when CS_2 and paraffins are present, the percentages of benzene and toluene may be calculated as follows:—The total volume of benzene and toluene present is 100–C–P. Then if B^1 and T^1 are the percentages of benzene and toluene found by Graph 1 from the percentage distilling to 85°, and B and T the true percentages of benzene and toluene corrected for paraffins and carbon bisulphide present,

$$B = (100-C-P)\,(B^1 - C) \div (100-C),$$
$$T = (100-C-P)\,T^1 \div (100-C).$$

With most products from tar consisting chiefly of benzene, the percentage of paraffins and CS_2 present is comparatively small, that of carbon bisulphide being mostly from 0·5 to 1·5 per cent., and that of paraffins not exceeding 5–6 per cent. being in the majority of cases much less; in such samples the percentage of benzene and toluene corrected for these may be obtained with sufficient accuracy by a simpler calculation, namely, by multiplying the percentages of those found by Graph 1 by 100 minus the combined percentages of carbon bisulphide and paraffins found by Graph 2, and dividing by 100, in which case

$$B = B^1 \times (100-C-P) \div 100, \text{ and}$$
$$T = T^1 \times (100-C-P) \div 100.$$

With only such amounts of carbon bisulphide and paraffins present, the figures obtained by the shorter method differ only by fractions of 1 per cent. from those found by the longer method, *i.e.* by an amount which is smaller than the unavoidable experimental errors. The longer method is only necessary with products such as the "fore-runnings" collected in large scale distillation previous to collecting "commercial" benzol containing much CS_2[1] and with products containing very high proportions of paraffins, such as are sometimes obtained from vertical retort tars, or from the low temperature carbonisation of coal.

Commercial Benzol.—Samples of commercial benzol may be analysed by the method given for the "fraction up to 90°" previously described, but in certain cases slight modifications are advisable, namely, if (1) the percentage of toluene present is less than 3–4 per cent., and (2) if the percentage of toluene is high.

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[1] See Spielmann and Butler-Jones, *J.S.C.I.*, 1916, 911.

Where the percentage of toluene is below 3-4 per cent., the method is slightly modified by distilling to 85° a mixture of 95 c.c. of the sample with 5 c.c. of pure toluene. From Graph 1 the percentage of toluene in this mixture is read off from the percentage distilling to 85°, and this figure minus the 5 c.c. of toluene added, multiplied by 100 and divided by 95, gives the percentage of toluene in the original sample, the difference between this figure giving the percentage of benzene in the sample, if carbon bisulphide and paraffins are absent. The corrections for these are ascertained as specified above.

Where the percentage of toluene is high, this is mostly accompanied by small quantities of xylene, and in the test such xylene counts as an equal amount of toluene. For many purposes this is immaterial, and the results given by the test are correct if the figure given for toluene is recorded as "toluene + xylene." If it is desired to ascertain the separate percentages of toluene and xylene, 500 c.c. of the sample is distilled with a Young 12-bulb pear column, the fraction "up to 90°" analysed as above, and the residue at 90°, consisting of benzene, toluene, and xylene, analysed by the method given below for the "fraction 90°–140°." With a product such as the commercial 50/90's benzol, which always contains considerable amounts of xylene, this procedure is always advisable.

Unwashed Benzol.—In some works it is the practice to fractionate the crude naphtha previous to washing with acid, etc., and then to subject the unwashed benzol and unwashed toluol separately to the washing process.

To analyse such a sample of unwashed benzol it is washed with 8 per cent. of its volume of concentrated sulphuric acid, in the manner previously described. The washed spirit is transferred to a round-bottomed flask fitted with a tube for introducing steam, and distilled with steam as already described. The distillate after removal of water is analysed by the method just described, due allowance being made for the loss on acid washing in calculating the percentages of benzene, toluene, carbon bisulphide, and paraffins in the original unwashed sample.

Fraction 90°–140° C. and Commercial Toluol.—The principle upon which the determination of the percentages of benzene, toluene, and xylene in such samples is carried out is as follows:—When the distillation of mixtures of these hydrocarbons in known proportions is carried out in the same apparatus and under the same conditions as described for the "fraction up to 90°," it has been found that the percentage of the distillates obtained between fixed ranges of temperature is quite constant, and that if a graph be drawn up in which the percentages boiling below a fixed temperature are plotted as ordinates, and the percentages of residue at a high fixed temperature as abscissæ, the points on the graph correspond to the known percentages of benzene and toluene in the mixture lie on regular curves. From the results obtained in a large number of distillations of mixtures containing varying but known amounts of pure benzene, toluene, and xylene, and measuring (1) the percentage boiling up to 105° corr. and (2) the residue left at 116° corr., Graph 3 has been plotted in the manner mentioned, the continuous line curves giving the percentage of toluene and the broken line curves the percentage of benzene corresponding to the percentages of distillate up to 105° and above 116°. With a mixture of benzene, toluene, and xylene in unknown quantities the percentages of distillate up to 105° corr. and above 116° corr. are ascertained, and the percentages of benzene and toluene present may then be directly read off on Graph 3 from the broken line curves and full line curves respectively. The percentage of xylene is found by difference. There seems no reason why a similar method should not be employed for determining three successive members of any homologous series provided that they do not form constant boiling mixtures and that their boiling points are not too close together.

Note.—In the method as originally published, the temperatures for the interruption of the distillation were taken as 105° and 117°, and for special reasons, which were only of a temporary nature, the thermometer graduated with complete immersion of the stem, and an approximate correction for barometer and unheated stem employed. For several reasons it has been found better to employ a thermometer graduated with 100 mm. immersion to avoid the necessity of making any correction for unheated stem, which makes slight alterations in the form of the graph, and in order to avoid confusion between the old and the new graphs the latter was drawn up for a different temperature interval.

The method with the specified interruption points of 105° and 116° only holds generally for samples containing 50-75 per cent. of toluene and for such as give at least 5 per cent. of distillate up to 105° and 5 per cent. above 116°. Samples which do not fall within these limits can, however, be readily analysed by the method by adding to them such known amounts of pure benzene, toluene, or xylene as bring the mixture within these limits, and distilling the mixture under the standard conditions. From the percentages of benzene, toluene, and xylene found in the mixture, and from the known amounts of benzene, toluene, or xylene added to it, the percentages of the hydrocarbons in the original samples are readily calculated.

If in addition to xylene small quantities of cumenes or similar higher boiling aromatic hydrocarbons are present, the results obtained by the test are unaffected, except in so far that the difference figure between 100 and the percentages of benzene plus toluene then gives the percentage of xylene plus higher boiling aromatic hydrocarbons instead of that of pure xylene.

Carbon disulphide, if present in the sample in more than a small amount, renders the results less accurate, but it is never present in appreciable amount in the fraction 90°–140° prepared as described. Commercial products, such as 50/90's benzol, may contain more of this impurity, but such samples, as already mentioned, should first be distilled into a fraction up to 90° and residue at 90°, and the two fractions analysed separately.

Paraffins, when present, affect the results somewhat, but a correction for the error thus caused and an estimation of the percentage of paraffin present can be ascertained from the specific gravity of the sample in the manner described later.

Method of Distillation.—As in the case of the fraction "up to 90°," "100 c.c. of the fraction 90°–140° is distilled from the standard Engler flask at the rate of about 7 c.c. per minute. When the thermometer shows a temperature of 105° corr. the distillation is stopped, the condenser allowed to drain, and a fresh cylinder placed under the condenser. The distillation is then continued under the same conditions until the thermometer shows a temperature of 116° corr., when the distillation is again interrupted. The residue, after cooling, is poured into a third cylinder, and the contents of the three cylinders are measured at a temperature approximating to that of the 100 c.c. taken for analysis. The total volume of the three fractions up to 105°, 105°–116°, and above 116°, should not amount to less than 99·5 c.c.

In the absence of paraffins, the percentages of benzene and toluene are directly read off from the percentages below 105° and above 116° by means of Graph 3.

If, as the result of the distillation, values for the fractions up to 105° and above 116° are obtained which give no value for benzene and toluene on Graph 3, owing to the composition of the sample being such that it does not fall within the limits already specified, a further portion of the sample is taken less than 100 c.c. and made up to 100 c.c. with a known amount of pure benzene, toluene, or xylene. The quantities of these which it is necessary to add vary according to the composition of the sample, but with a little practice it becomes very easy to estimate the amounts which should be added. The following are examples frequently met with :—

(1) The percentage of the sample boiling either up to 105° or above 116° may be below 5 per cent. In this case 90 c.c. of the sample is taken and mixed previous to distillation with 10 c.c. of benzene, if the distillate up to 105° was below 5 per cent., or with 10 c.c. of xylene if the residue above 116° was below 5 per cent. Thus, if the first test showed less than 5 c.c. below 105°, and a mixture of 90 c.c. of the sample with 10 c.c. of benzene gave 10 c.c. to 105° and 21 c.c. above 116°, then from Graph 3 the amount of benzene in the mixture is 15 per cent., and that of toluene 72 per cent. As 10 c c. of benzene was added, the 90 c.c. of the original sample contains 15 – 10 = 5 c.c. of benzene and 72 c.c. of toluene, whence, in the original sample benzene = 5 × 100 ÷ 90 = 5·5 per cent.; toluene = 72 × 100 ÷ 90 = 80·0 per cent. ; xylene = 100 – 5·5 – 80 = 14·5 per cent.

(2) The percentage boiling both below 105° and above 116° may be below 5 per cent In this case 80 c.c. of the sample may be mixed with 10 c.c. of benzene and 10 c.c. of xylene, or if the percentage of toluene is very high, 75 c.c. of the sample is mixed with 15 c.c. of benzene and 10 c.c. of xylene. The percentage of benzene found in the mixture, less the quantity of benzene added, and that of toluene found (without deduction) multiplied by the number of c.c. of original spirit taken and divided by 100, then gives the percentages of benzene and toluene in the original, that of xylene being found by difference.

(3) The percentage boiling above 116° may be so high that no reading can be obtained on the graph. With this class, 80 c.c. is mixed with 20 c.c. of benzene and the mixture analysed, the percentages of benzene, toluene, and xylene in the original sample being calculated in a similar manner.

(4) The percentage boiling below 105° may be so high that no reading can be obtained on the graph. In such cases, which include samples with rather high percentages of benzene, and in many cases the fraction "90°–140°" obtained as specified above, 80 c.c. of the sample is mixed with 20 c.c. of toluene. Where the percentage of benzene is very high, the mixture of 80 c.c. with 20 c.c. of toluene may still contain below 50 per cent. of toluene. This rarely occurs with the fraction 90°–140° obtained as specified, but may happen with products such as 50/90's commercial benzols. In such cases a smaller volume of the original and a larger amount of toluene may be taken, but the smaller the proportion of the original taken the greater is the unavoidable experimental error in the results. Where results are desired as accurate as possible, and the quantity of the sample available permits of it, it is then better to distil 250 c.c. of the sample with a column into the fractions "up to 90" and "above 90." and to analyse these separately, the first by the method given above for the fraction "up to 90°," and the second by that for the fraction "90°–140°."

Paraffins in Fraction 90°–140°.—The results obtained in the manner described give the percentage of benzene, toluene, and xylene, on the assumption that no paraffins are present. When these are present, they count in the test as aromatic hydrocarbons, and thus bring about an error in the results. From blank tests made with mixtures of the three aromatic hydrocarbons with paraffins, it has been found that when the percentage of paraffins does not exceed 5–7 per cent. no material error is caused by assuming that the result for each of the three aromatic hydrocarbons is affected in proportion to the total percentage of paraffins present, and that the true percentages of benzene, toluene, and xylene may be obtained by multiplying the "uncorrected" percentages found as above by 100 minus the percentage of paraffins present and dividing by 100.

The percentage of paraffins present may be found with a fair degree of accuracy, from the specific gravity of the sample, in a manner similar to that employed in the case of the benzene fraction. The specific gravity of a mixture of benzene, toluene, and xylene of the "uncorrected" percentages found can be calculated from the specific gravity of pure benzene, toluene, and xylene.

If there were no expansion or contraction occurring when benzene, toluene, and xylene are mixed, and also no expansion or contraction on the addition of paraffins to this mixture, then if a is the calculated specific gravity of paraffin-free mixture, b the observed specific gravity of the sample, and c the specific gravity of paraffins present, the percentage of paraffins present would be

$$100 \times (b-a) \div (c-a).$$

But, in fact, expansion occurs both when benzene, toluene, and xylene are mixed and also on addition of paraffins to these mixtures. If k^2 is the fall in specific gravity due to expansion on mixing benzene, toluene, and xylene, and k^3 the further fall on addition of paraffins to this mixture, then

$$\text{Paraffins per cent.} = 100 \times \frac{\{[b+(k^2+k^3)]-a\}}{\{c-(a+k^2)\}}$$

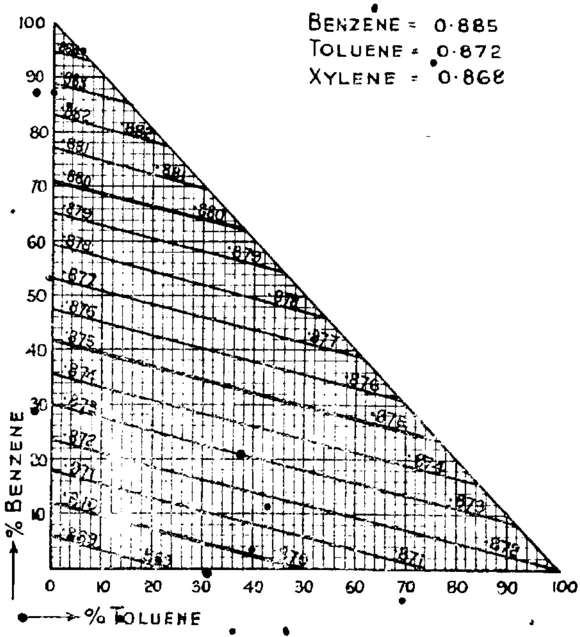
The value of k^2 varies somewhat, but within the range of the proportions of benzene, toluene, and xylene usually present in the fraction 90°–140° or in commercial toluol, it may be taken as having a constant value of 0·0010. The value of k^2+k^3 for the combined fall in specific gravity on mixing benzene, toluene, xylene, and paraffins has been found experimentally as an average value as follows:—

Paraffins per cent.	k^2+k^3.
1	0·0012
2	0·0014
5	0·0019
10	0·0022
15	0·0025
20	0·0030

The average value of the specific gravity of the paraffins present in this fraction may also vary, but has been found by isolating them to be usually about 0·74, which is taken as the value of c.

The specific gravity of benzene, free from paraffin hydrocarbons, is 0·885. With regard to the specific gravity of pure toluene authorities differ. The figure is usually given as 0·870, which is rarely exceeded in samples of commercial "pure toluene" obtained from coal-tar. W. H. Perkin, senior, however[1] showed that when such toluene is converted into the sulphonic acid and the latter purified and reconverted into toluene, the hydrocarbon thus obtained, absolutely free from paraffins, has the specific gravity of 0·8721, and a repetition of his work has confirmed this figure. The specific gravity of toluene, free from paraffins, is therefore taken as 0·872.

In the case of xylene, the specific gravity is in any case uncertain, as this is a mixture of o-, m-, and p-xylene, each of which has different boiling point and different specific gravity. Perkin found the specific gravity of these three xylenes, when pure, to be:—o-xylene 0·8818, m-xylene 0·8691, and p-xylene 0·8661; as the mixtures of xylenes from coal tar, etc., usually consist to the largest extent of m-xylene, with a smaller amount of p-xylene, and still smaller amounts of o-xylene, the average specific gravity of the xylene mixture entirely free from paraffins may be taken as 0·868. Commercial "pure xylene" rarely has a higher specific gravity than 0·865-0·866, and like the commercial "pure toluene" still contains small amounts of paraffins.



GRAPH 4.—Calculated Specific Gravity of Paraffin free Mixtures of Benzene, Toluene, and Xylene.

Having obtained the "uncorrected" percentage of benzene, toluene, and xylene in the sample in the manner already described, and also the specific gravity of the sample, the percentage of paraffins is determined as follows:—from Graph 4 the calculated specific gravity of the mixture is read off from the percentages of benzene and toluene found (the specific gravity of the pure hydrocarbons being taken as 0·885, 0·872, and 0·868 respectively), and the percentage of paraffins is then read off from the observed and calculated specific gravities by means of Graph 5, which is drawn up from the formula given, allowing for the expansions which occur. The "corrected" amounts of benzene, toluene, and xylene are then obtained by multiplying the "uncorrected" figures by 100 minus the percentage of paraffins, and dividing by 100.

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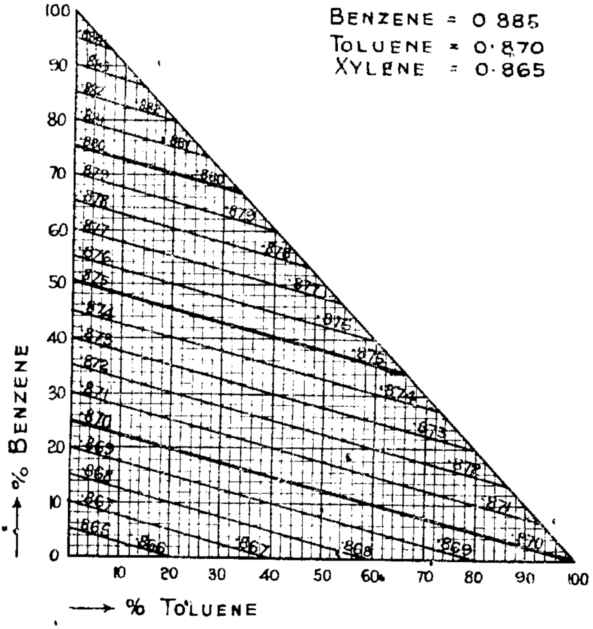
[1] *J. Chem. Soc.*, 1896, 1191.

For many purposes it is frequently desired to ascertain the percentage present, not of the true paraffin-free toluene or xylene, but that of the percentages of ordinary "commercially pure toluene" of specific gravity 0·870 and of "commercially pure xylene" of specific gravity 0·865. To enable these percentages to be ascertained readily, Graph 4A has been drawn up in exactly the same manner as 4, but taking the specific gravity of toluene as 0·870 and of xylene as 0·865, and the readings obtained from these Graphs, 4A and 5, give directly the percentages of commercially pure toluene of specific gravity 0·870 and commercial xylene of specific gravity 0·865. The percentage of paraffins, of course, then comes out slightly less, as a small amount of these is included in the "commercially" pure toluene and xylene.



GRAPH 4A.—Calculated Specific Gravity of Paraffin-free Mixtures of Benzene, Toluene, and Xylene.

As previously stated, when the percentage of paraffins exceeds about 7 per cent., the "uncorrected" figures obtained for benzene, toluene, and xylene are not necessarily in proportion to the true percentages present, and the "corrected" figures obtained in the manner specified may be in error to the extent of 2-3 per cent. With most coal-tar products, the percentage of paraffins rarely exceeds 5 per cent., but in certain samples, such as the products from coal-tar obtained in vertical retorts, the percentage may rise to 20 per cent., and is often still higher with products obtained by very low temperature carbonisation.

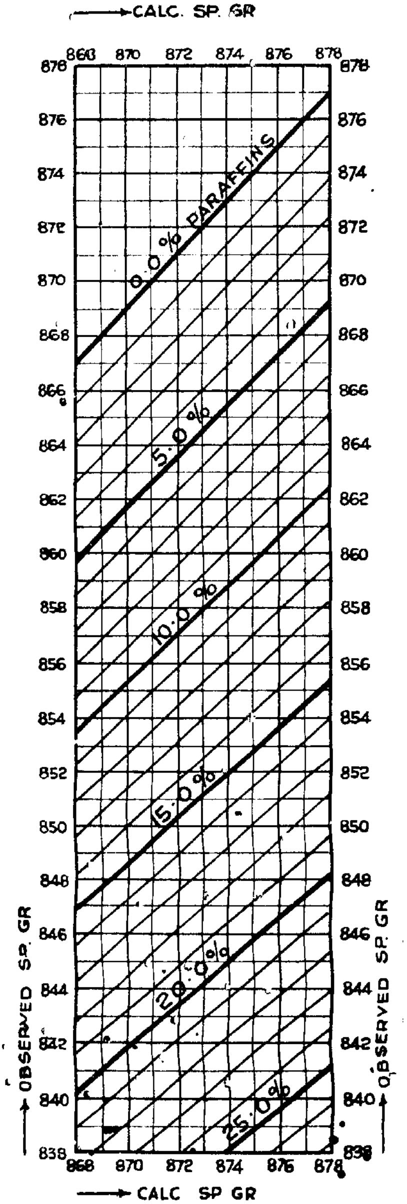
Blank tests with known mixtures of the aromatic hydrocarbons containing up to 10-25 per cent. of paraffins have shown that this error may be greatly reduced, if in the distillation of the fraction "90°-140°" such quantities of benzene, toluene or xylene are added to it that the mixture contains between 52 and 58 per cent. of toluene uncorrected for paraffins, and on distillation gives not less than 20 per cent. respectively of distillate up to 105° and residue "above 116°." For percentages of paraffins above 25 per cent., whilst the method gives fairly accurate figures for the percentage of paraffins, no method has been found whereby it is possible to get accurate determinations of the percentages of benzene, toluene, and xylene present.

Unwashed Toluol.—In some cases in works practice the toluol fraction is separated by distillation from the crude naphtha previous to acid washing. For the analysis of such samples, 150-250 c.c. of the spirit is washed with acid and steam distilled in the manner described for unwashed benzol previously described. If the percentage of xylene is not required, instead of steam-distilling the residual oil after treatment with sulphuric acid, etc., this may be distilled without steam, using a good column, and collecting the distillate to 140° (adding a little xylene if the thermometer does not reach 140°) and making up the distillate with pure xylene to the volume of unwashed toluol originally taken.

Fraction 140°-160°, and Commercial Solvent Naphtha.—The fraction 140°-160°, obtained from the preliminary distillation of coal-tar, etc., in the manner described, consists of the constituents present in commercial coal-tar solvent naphtha, namely, xylenes, cumenes, and other aromatic hydrocarbons of boiling points up to about 170° C. If to the percentage of this fraction found there is added the percentage of xylene (calculated on the original tar) found in the fraction 90°-140°, the combined figures give an approximate estimation of the quantity of commercial solvent naphtha contained in the tar.

Owing to the large number of hydrocarbons present, and the fact that the boiling points of the constituents are in many cases so near together, it is not possible by any distillation method to make any determination of the relative amounts of the individual constituents. The composition of the commercial products varies considerably, but when prepared from crude tar fairly free from paraffin hydrocarbons, its specific gravity is usually from 0·865 to 0·866. Each 0·001 that the specific gravity of a sample of xylene or solvent naphtha is found below 0·868 indicates the presence of approximately 1 per cent. of paraffins. The commercial product also often contains a higher percentage of unsaturated hydrocarbons than is the case with commercial benzol and toluol, since for many purposes for which solvent naphtha is employed the complete removal of these is unnecessary, and therefore the acid washing to which it is subjected in practice is less severe.

Benzene and Toluene in Commercial Solvent Naphtha.—The commercial product mostly contains varying amounts of toluene, and in addition sometimes contains small quantities of benzene. To determine with accuracy the amount of these hydrocarbons present, 250 c.c. of the sample is



GRAPH 5.—Percentage of Paraffins in Fraction 90°–140° and in Comm. Toluol

distilled with a good column at the rate of about 4 c.c. per minute, and the distillate to 142° collected. This first distillate is then again fractionated in the same apparatus, the distillate being now collected to 138° and its volume measured. This second distillate is essentially identical with a commercial toluol, rather high in xylene and low in benzene content, and is analysed by the method given above, the quantity of benzene and toluene found being calculated to percentages of the original solvent naphtha.

A quicker method, giving results sufficiently accurate for many purposes, is to distil 100 c.c. of the sample with a column, the distillate to 138° being collected in a 100 c.c. cylinder. To this is added 20 c.c. of benzene, and the contents of the cylinder then made up with toluene to 100 c.c. This mixture is then distilled, and the fractions "up to 105°" and above 116° determined, and the percentages of benzene and toluene in the mixture read off on Graph 3. The percentage of benzene found in the mixture, less the 20 c.c. added, and the percentage of toluene found, less the amount added to make up 100 c.c., give directly the percentages of benzene and toluene in the original solvent naphtha.

Fraction 160°–200°.—The amount of this fraction, obtained from the original preliminary distillation of the tar or oil, gives an approximate figure of the amount of "heavy solvent naphtha" contained in the tar. Commercial heavy solvent naphtha, like the light solvent naphtha, consists chiefly of aromatic hydrocarbons, but in the heavy naphtha the boiling point of these lies mainly from 160° to 200°. Any paraffins of similar boiling point present in the original tar are also contained in this fraction. As with solvent naphtha, the number of constituents is so large and their boiling points so close together, that their estimation by any distillation method is impracticable. The specific gravity of the fraction from different tars also varies so much that even an approximate estimation of the percentage of paraffins present is hardly practicable by this means.

Degree of Accuracy of Method.

During the past four years some hundreds of blank tests have been made of mixtures made up with known amounts of pure benzene, toluene, xylene, carbon bisulphide, and paraffins in order to determine the degree of accuracy which may be expected in the analysis, especially of the fractions "up to 90°" and "90°–140°" corresponding to commercial benzol and commercial toluol.

In the case of the fraction "up to 90°" when this consists of benzene and toluene only, the figures obtained show that when using an accurately calibrated thermometer and adhering to the conditions specified, the results given by the analysis differ only from the quantities actually taken by less than 0·5 per cent., and even when paraffins are present, unless their percentage is high, the results rarely differ from the true figures by more than that amount. The percentage of carbon bisulphide usually comes out correct within 0·1 per cent.

With the fraction 90°–140°, and in properly washed commercial toluol, in the absence of paraffins, the results obtained for all three constituents, benzene, toluene, and xylene, are almost always within 0·5 per cent. of the true figures. A series of 140 tests of mixtures of known amounts of pure benzene, toluene, and xylene, in which the relative amounts were varied as much as possible, showed that of the 420 separate determinations of the three constituents, none differed from the correct figure by 1 per cent., and in only six cases was the error more than 0·5 per cent. The average quantities of benzene, toluene, and xylene in the 140 mixtures taken were as follows:—Benzene 21·4 per cent., toluene 61·7 per cent., xylene 16·9 per cent., and the average quantities found were identical, the errors in the individual tests balancing each other.

With quantities of paraffins not much exceeding 5 per cent., the experimental error is slightly greater, but rarely exceeds 1 per cent. With higher percentages of paraffins the possible error increases, but if the precaution is taken previously mentioned with regard to the composition of the actual mixture distilled to determine the percentages boiling below 105° and above 116°, the error rarely much exceeds 1 per cent. up to 25 per cent. of paraffins, though in the absence of this precaution the error in the percentage of toluene present may rise to 3 per cent. Above 25 per cent. of paraffins the magnitude of the possible error increases considerably

The length of time required for the preliminary distillation of the tar or oil varies considerably according to the quantity of the latter which has to be taken to give a sufficient quantity of the light fraction for the further analysis, and also, as is well known, especially according to the amount of water and solid matter ("free carbon") in the tar. The further complete analysis of the unwashed fraction to 200° takes from 3½ to 4 hours, but if the analysis of two or more samples is carried on simultaneously, the average time required is considerably less

In the subjoined schedule, the detailed results are given resulting from the analysis of a "crude benzol" from gas made in vertical retorts, containing carbon bisulphide and a somewhat large percentage of paraffins, which exemplifies the carrying out of the method and the necessary calculations:—

ANALYSIS OF CRUDE BENZOL FROM VERTICAL RETORTS.

Volume taken for analysis, 500 c.c., specific gravity at 15·5° C. = 0·854 :—

Original sample.

Distillate to 200°	462 c.c.
Residue at 200° (diff.)	38 ,,

Unwashed fraction to 200°.

Vol. after alkali washing	45[illegible]c.
Loss	4 ,,
Vol. after acid washing	420 ,,
Loss	38 ,,

Fractionation of washed distillate.

		Specific gravity.
Up to 90°	160 c.c.	0·856
90°–140°	147 ,,	0·840
140°–160°	37 ,,	0·824
160°–200°	30 ,,	0·840
Residue at 200° by diff.	46 ,,	—

Washed distillate "up to 90°."

100 c.c. gave 83·3 c.c up to 85°.
From Graph 1. Benzene = 90·0% unc.,
Toluene = 10·0% „
Specific gravity before CS_2 removal, 0·856
„ „ after „ 0·854
From Graph 2. CS_2 = 0·5%. Paraffins 17·2%.

	% Comp. of fraction.	Comp. of 160 c.c.
CS_2	0·5	0·8 c.c.
Paraffins	17·2	27·5 „
Benzene	74·1	118·6 „
Toluene	8·2	13·1 „

Washed distillate, 90°–140°.

81 c.c. + 19 c.c. Toluene + 0 c.c. Benzene.

		From Graph 3.
Up to 105°	39·8%	Benzene = 29·3 per cent.
105°–116°	35·3%	Toluene = 53·6 „ „
Above 116°	24·5%	Xylene = 17·1 „ „

	In 81 c.c. of w.d. 90°–140°.	In 100 c.c. of w.d. 90°–140°.
Benzene, unc	29·3	36·2
Toluene, unc.	34·6	42·7
Xylene, unc.	17·1	21·1

Specific gravity of fraction . . . . . 0·840
Calc. specific gravity of paraffin-free sample from Graph 4 0·876
Therefore, from Graph 5 paraffins = 24·7 per cent.

	% Comp. of fraction.	Comp. of 147 c.c. of fraction.
Paraffins	24·7	36·3 c.c.
Benzene	27·2	40·1 „
Toluene	32·2	47·3 „
Xylene	15·9	23·3 „

In order to check, as far as possible, the accuracy of the results, a mixture was made up of the number of c.c. found of CS_2, petrol (free from aromatic hydrocarbons) boiling from 80° to 140°, pure benzene, pure toluene, solvent naphtha free from toluene, and heavy naphtha To the naphthas, however, were previously added paraffins of similar boiling point to make their specific gravity approximately 0·83 and 0·84 This mixture was then analysed in the prescribed manner, the following results being obtained :—

	Taken %.	Found %.
CS_2	0·2	0·2
Paraffins [illegible]	17·1	16·5
Benzene	42·2	43·3
Toluene	16·2	16·5
Solvent naphtha	16·2	14·1
Heavy naphtha	8·0	9·4

	Fraction up to 90°.	Fraction 90°–140°.	Fraction 140°–160	Fraction 160°–200°.	Loss on Alkali Washing.	Loss on Acid Washing	Fraction over 200° Washed Distillate.	Fraction over 200° Original.	Total in 500 c Original.	Per Cent. of Original.
CS_2	0·8	...	...			...		...	0·8	0·2
Paraffins to 140°	27·5	36·3	...	...	...	...		...	63·8	12·8
Benzene	118·6	40·1	...	...	...			...	158·7	31·7
Toluene	13·1	47·3	...	...	...	...	...	...	60·4	12·1
Solvent naphtha		23·3	37·0		...	...	...	...	60·3	[1] 12·0
Heavy naphtha	...	...	...	30·0	...	...	...	...	30·0	[1] 6·0
Loss on alkali wash	...		...		4·0		...	...	4·0	0·8
Loss on acid wash	...			...	...	38·0	...	...	38·0	7·6
Above 200° washed distillate	...			...	...	...	46·0	...	46·0	9·2
Above 200° in original	...	...		...	...	...	...	38·0	38·0	7·6

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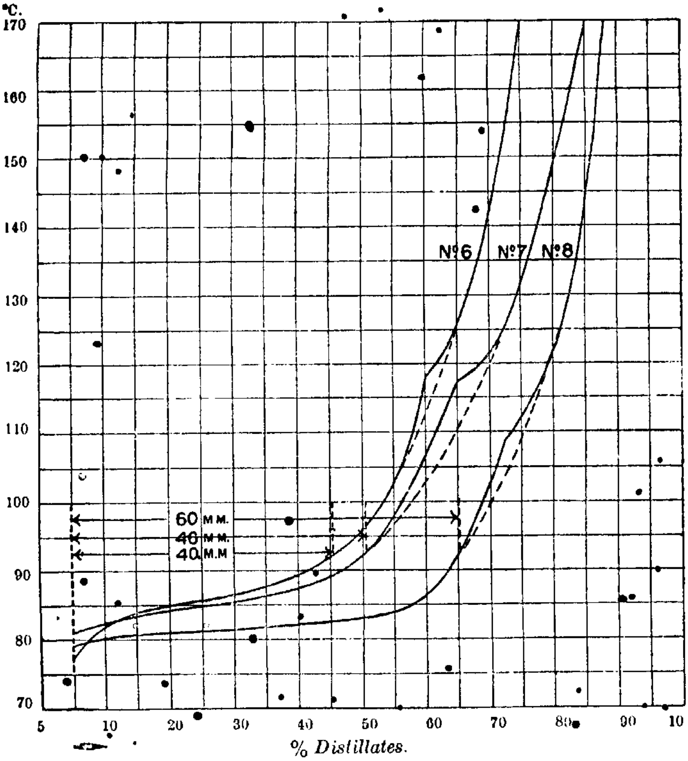
[1] These contain approximately 40–45 per cent. paraffins.

Another Method.

The following method of analysis of crude benzol is suggested by Spielmann and Petrie[1] to replace the obsolete retort test, which from a scientific point of view is totally inadequate to meet the requirements of modern Benzol Work practice.

Another mode of examining crude benzols, yielding appreciably accurate results, is to distil at least a litre over a Young 12-pear head, and to note the rise of temperature for every 5 or 10 per cent. passing over. In Graph 6 three such curves are shown, quite ordinary and characteristic of the operation, which indicate from their shape that there is a considerable quantity of benzene and some toluene present; but how much is not obvious—it is not immediately clear how the curve is to be interpreted quantitatively.



Graph 6.

Benzene Estimation.—It has been found that when such curves are plotted in the manner shown on mm. paper (Graph 6) the horizontal distances between the 5 per cent. mark and the point where the curve cuts the 92·5° C. line gives a close measure of the percentage of benzene present.

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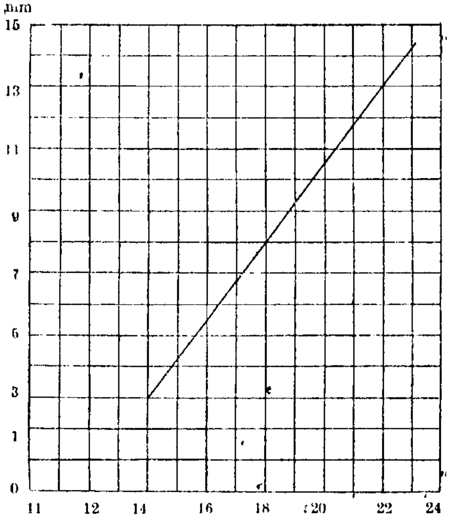
[1] *J.S.C.I.*, 4th June 1917.

Example—

No.	From Curve.	By Analysis.
	Per Cent	Per Cent.
4.	50	52
5.	67	66
6.	40	38
7.	46	46
8.	60	58
9	40	36

Toluene Estimation.—Further, it has been found that the quantity of toluene is proportional to the number of mm. of maximum deviation of the experimental curve from the smoothed curves shown dotted on the graph



% *Toluene*

GRAPH 7.

This relationship is read off by means of Graph 7.

Example—

No.	Deviation mm.	Toluene.	
		From Curve.	By Analysis
4.	3·8	14·6	14·9
5.	3·5	14·0	14·0
6	4·0	15·0	16·0
7·	8·0	18·0	19·0
8.	5·5	16·0	13·0
9.	13·0	22·0	22·0

COMMERCIAL BENZOLS.

New Distillation Test for Benzol, to meet Government Requirements.

The object is to test washed benzol in such a manner as to ensure that it does not contain more than a stipulated proportion of toluene.

The specification is modelled on that of the well-known "retort" test.

A distillation flask is used, having a side tube in the neck. The bulb of the flask is of sufficient capacity (about 150–180 c.c.) conveniently to distil 100 c.c. The neck should be about 4·5 inches long, and the side tube should be at about the middle of the neck.

Before making the test, the condenser tube and the flask should be washed out with a little of the sample that is to be tested, and allowed to drain thoroughly. A measuring cylinder, graduated in cubic centimetres, is filled up to the 100 c.c. mark, and the liquid poured from this into the flask. The flask is connected by a cork to an efficient condenser, the graduated cylinder already used being employed, without drying, for collection of the distillate.

The sample must be at the temperature of the laboratory when the above 100 c.c. are measured out.

The rate of distillation should be 2 drops per second from the delivery end of the condenser.

The position of the thermometer should be such that the top of the bulb is ½ inch below the side tube of the flask.

The thermometer must be accurate, or its error must be known and allowed for.

Allowance must be made for the barometric reading, the temperature being taken 0·1° higher than that required for each 0·1 inch by which the barometer reading exceeds 30 inches; and the distillation stopped 0·1° below the required temperature for every 0·1 inch below 30 inches

The apparatus must be sheltered from draughts during the distillation.

The source of heat should be the naked flame of a spirit lamp or bunsen burner (the rose must not be used). The flame should be protected by a small cylinder of wire gauze of about 2 inches diameter.

The flame is extinguished when the thermometer indicates the required temperature, allowing for the above corrections. The apparatus is allowed to cool; the quantity of distillate is noted, and the residue remaining in the flask is then drained into the liquid in the receiving measure, any shortage from 100 c.c. due to "loss on distillation" being added to the already observed volume of distillate.

THE ANALYSIS OF COMMERCIAL BENZOLS.[1]

Method of Spielmann and Wheeler.

Determination of Toluene.—It has been found that if 100 c.c. of a mixture of benzene and toluene be distilled from an Engler flask at the rate of 7 c.c. a minute, with proper precautions with regard to draughts and efficient condensation of the distillate, the volume in c.c. passing over up to 90° C. indicates the quantity of toluene present in the mixture when reference is made to a previously constructed curve. It has been found, further, that the presence of paraffin and carbon bisulphide in the quantities normally occurring in commercial benzols does not upset this relationship to any material degree.

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[1] *J.S.C.I.*, 15th April 1916.

The method is not to be trusted above 20 per cent. of toluene, because the errors which ordinarily balance one another in any chemical manipulation may, if acting all in one direction, cause an error of 2 per cent or more. Thus, the increasing inaccuracy with increasing quantities of toluene carries the method into the region of others for the estimation of toluene, such as that of Colman,[1] and of Northall-Laurie,[2] which, from this point onwards, show a greater accuracy the higher the percentages of toluene present.

Experience has shown that the estimation of the toluene by the distillation method just described may vary in the hands of different workers with slightly differing apparatus, to the extent of 2 per cent. Although such a discrepancy is in itself undesirable and can be rectified, it does not have any appreciable effect in the subsequent estimation of paraffin.

Determination of Carbon Bisulphide.—Carbon bisulphide is easily and completely removed by alcoholic potash in the known manner; but instead of the potassium xanthate being estimated, the benzol is washed several times with water, in order to remove the xanthate and alcohol, and dried: its specific gravity is then determined. The difference between the original specific gravity of the sample and the specific gravity just obtained is proportional to the quantity of carbon bisulphide present, and this can be found by reference to a previously constructed curve.

This method has been suggested by Nickels[3] and by Ellerton.[4] The slope of the curve in Graph 8 is given by the constant 0·002816, a slightly different figure from the 0·00346 found by Ellerton.

Determination of Paraffin.—After the removal of carbon bisulphide the liquid consists substantially of a mixture of benzene, toluene, and paraffin. The quantity of toluene has already been determined, and the specific gravity of a mixture of benzene and the ascertained quantity of toluene can be found from a previously constructed curve, so that the difference between the specific gravity of the benzene-toluene mixture and that of the sample after removal of carbon bisulphide is proportional to the quantity of paraffin present, the actual value of which can be found from an experimental curve.

Originally there was some doubt as to the proper specific gravity to ascribe to the paraffin occurring in benzols. This must certainly vary with the varying quality of coal distilled, as well as with the character of the retorts and the temperature of the destructive distillation. From actual analysis and from theoretical considerations, this has been taken to be 0·730. As a matter of fact, it has been found by experiment that the gravity may vary 0·025 without seriously upsetting the results obtained.

Determination of Benzene.—This constituent is estimated by difference. The work has been based on the specific gravity of benzene being 0·8848 at 15·5° C., a figure which has been obtained from synthetical benzene, boiling constantly at 80·2° C.

The graphs, however, have been drawn for a specific gravity of 0·8850 at 15·5° C. To a certain extent the unimportant impurities present in benzols will tend to balance one another with respect to their specific gravities, but with an upward tendency.

The most important of these impurities is thiophene, but this is seldom present to an amount of more than 0·5 per cent. (Lunge), and averages about 0·26 per cent.[1]

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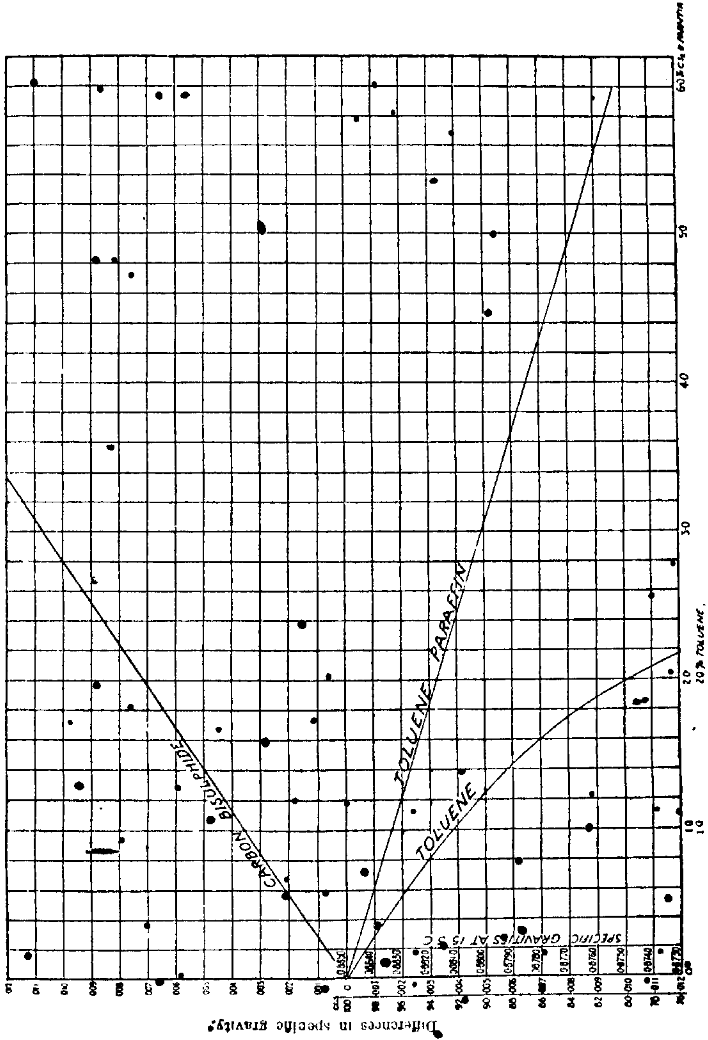
[1] Page 83.

[2] Page 114.

[3] Allen's *Commercial Organic Analysis*, 1900. vol. ii., pt. 2, p 183.

[4] *J.S.C.I.*, 1912, p. 11.

The latter quantity would cause an error of 0·3 per cent. in the quantity



GRAPH 8.

of paraffin found, but as this is within the limits of accuracy of the method it can be neglected.

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[1] Schwalbe, *Z. Farben- u. Textil-Ind.*, 1905, **11**, 113.

From the analysis of a number of known mixtures and of commercial benzols the following can be quoted, the results being given in per cent. vol./vol.:—

Known Mixtures.

	Benzene %.		Toluene %.		Paraffin %.		Carbon Bisulphide %.	
	Taken.	Found.	Taken.	Found.	Taken.	Found	Taken.	Found.
A.	87·0	87·5	10·0	9·2	2·0	2·3	1·0	1·0
B.	84·0	84·5	10·0	6·8	4·0	4·3	2·0	2·0

Commercial Benzols.

	Distillation Test		Specific Gravity.		Paraffin %.	Carbon Bisulphide %	
	c.c.	Toluene %.	Original.	After Removing CS_2.		By Curve.	By Titration
1.	98·9	1·5	0·8875	0·8838	0·25	1·05	0·78
2.	91·2	11·1	0·8892	0·8840	..	1·45	1·34
3.	97·9	3·0	0·8866	0·8839	..	0·75	0·71
4.	98·6	2·0	0·8891	0·8857		1·00	0·93
5.	94·4	7·7	0·8872	0·8810	1·3	1·75	1·70

It will be seen that an average accuracy can be expected to the extent of toluene 1·0 per cent., paraffin 0·5 per cent., and carbon bisulphide 0·1 per cent., and that the extreme error is not serious.

A few preliminary experiments with "first runnings" show that this method of analysis can be applied with a slight modification.

In Graph 8 are collected in one diagram the curves showing the effects on the specific gravity of benzene, of toluene, carbon bisulphide, and paraffin, together with the toluene distillation curve. The method of employment is to find the percentage of toluene from the result of distillation, and then to pass up that ordinate until the benzene-toluene specific gravity line is met, at a point opposite which is found the specific gravity of such a benzene-toluene mixture. The differences of specific gravity, which have already been described as being proportional to the percentages of carbon bisulphide and paraffin, are read off from their respective curves.

Actually a slight error is introduced by thus obtaining the percentage of paraffin in a benzene-toluene-paraffin mixture and making no allowance for the carbon bisulphide removed from the original sample: the numerical difference is, however, too small to be of account.

Taking for example No. 3 from the above table:—

Distillation: 97·9 c.c. . . . = 3 per cent. toluene.
Specific gravity of original sample = 0·8866
Specific gravity after removal of CS_2 = 0·8839

Difference . . . . 0·0027 = 0·75 per cent. CS_2.

Specific gravity of benzene, 3 per cent. toluene . . . = 0·8840
Specific gravity after removal of CS_2 = 0·8839

Difference . . . 0·0001 = negligible % paraffin.

It is interesting to note in passing that the effect of toluene on the specific gravity of benzene is exactly one-tenth the effect of paraffin of the specific gravity of 0·730.

For the sake of convenience of working, the curves shown in Graph 9 have been plotted. Here it is not even necessary to determine the various differences in specific gravity: only the observed figures need to be dealt with. The analytical results are interpreted as follows:—

The number of c.c. distilling below 90° C. represents the percentage of toluene shown below. The number of c.c. distilling below 90° C. has been plotted against the specific gravity found after removal of CS_2, in such a manner that the percentage of paraffin is read off directly. The specific gravity of the sample has been plotted against the specific gravity after removing carbon bisulphide, whereby the percentage of the latter can be directly read off.

Taking as an example No. 5 from the above table:

Distillation: 94·4 c.c. . . . 7·7 per cent. toluene.
Specific gravity after removal of CS_2 = 0·8810
Junction of 94·4 c.c. ordinate and 0·8810 line is at 1·7 % paraffin.
Specific gravity of original sample = 0·8872
Specific gravity after removal of CS_2 = 0·8810
Junction of these two co-ordinates is at 1·75 per cent CS_2.

It may be of interest to follow the mathematical evolution of the one set of curves from the other.

The curves in Graph 8 have been found to have the following numerical characteristics:—

Distillation Curve.—It has been found that up to 8 per cent. of toluene (equivalent to 94·3 per cent. distilling below 90°) this is a straight line of the formula $D = 100 - 0{\cdot}7T$, where D = the percentage of c.c. below 90° and T = percentage of toluene.

Above 12 per cent. of toluene (equivalent to 90·6 per cent. distilling below 90° C.) the curve closely approximates to an exponential curve $D = 2{\cdot}034 - 0{\cdot}0063T$.

The "No-man's land" between these two curves is occupied by a line following the obvious general curvature.

Toluene Curve.—The variation in specific gravity of benzene by varying admixtures of toluene is found to follow the law, $T = 6060{\cdot}01\ (0{\cdot}8850 - g_1)$ where g_1 = the specific gravity of the benzene-toluene mixture.

Paraffin Curve.—This is expressed by $P = 606{\cdot}061\ (g_1 - g_2)$, where g_1 = the specific gravity of the benzene-toluene mixture, and g_2 = specific gravity after removal of CS_2.

Carbon Bisulphide Curve.—This is represented by $S = 281{\cdot}6\ (g - g_2)$ where g = original specific gravity of the sample, and g_2 = specific gravity after removal of CS_2.

The Graph No. 9 was obtained by plotting $g_2 = g - \frac{S}{281{\cdot}6}$

By uniting the formulæ representing the distillation curve with the paraffin and toluene specific gravity curves, the following expressions were obtained, which represent in graph 9 the percentage of paraffin as described earlier:

$D = 100 - 4242{\cdot}42\ (0{\cdot}8850 - g_2) + 7P$, up to 8 per cent. of toluene:
$\log D = 2{\cdot}034 - 38{\cdot}183\ (0{\cdot}8850 - g_2) + 0{\cdot}063P$, above 12 per cent. toluene.

Experiments have been carried out and Graph 10 elaborated by Spielmann and Jones,[1] in order to ascertain whether the above method for the analysis of commercial benzols is applicable *to first runnings*.

This fraction differs from the benzol fraction mainly in containing up to 10 per cent. or 15 per cent. (and rarely as much as 65 per cent.) of carbon bisulphide, and up to 15 per cent paraffin, together with very small proportions of a number of other substances.

From a known mixture it was found that even 65 per cent. of carbon bisulphide gave a distillation test corresponding to the amount of toluene added (5 per cent) within the limits of accuracy of the earlier benzol analysis.

It was found, further, that water soluble substances were insufficient in quantity to affect estimation by specific gravity, and also that a severe washing with sulphuric acid to remove other impurities did not cause alteration.

The method previously described can therefore be applied directly to the evaluation of benzol first-runnings with the following modifications:—

1. *Carbon bisulphide.*—The estimation of a high percentage of carbon bisulphide is most conveniently carried out by diluting the sample with up to five times its volume of benzene, which has been previously purified from any carbon bisulphide that it may contain.

2. *Paraffin.*—The specific gravity of the paraffin of this fraction is 0·700.

If the percentage of paraffin is such that it lies outside the graph, its quantity can be determined most easily by employing the simpler of the two benzol graphs (*loc. cit.*), ascertaining the specific gravity of benzene-toluene mixture by its means, and determining the difference between this and that of the sample under examination after removal of CS_2; the resulting difference is then evaluated by means of the paraffin graph.

Further, it becomes necessary to take into consideration the percentage of carbon bisulphide present and to correct the quantity of paraffin found by differences of gravities.

If, for instance, 10 per cent. of carbon bisulphide is present, the quantity of paraffin found will be that present in 90 c.c. of liquid, and the value, therefore, will have to be diminished in the ratio of 90 : 100.

In general, paraffin (true figure) = paraffin found multiplied by the fraction $\frac{100 - x}{100}$ where x is the percentage of CS_2.

This correction need not actually be calculated, as it can be obtained directly in graph 10.

The following examples of known mixtures indicate the mode of employment:—

(1) Mixture taken: 4 per cent. toluene, 3 per cent. paraffin, 12 per cent. CS_2, 81 per cent benzene.

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[1] *J.S.C.I.*, 15th September 1916.

Distillation of 100 c.c. up to 90° C. gives 97·5 c.c., equivalent to 3·6 per cent. toluene

Specific gravity after removal of CS_2, 0·8762.

Junction of 3·6 per cent. toluene with gravity 0·8762 line is at 4·3 per cent. paraffin.

Specific gravity of original sample, 0·9205.

Specific gravity after removal of CS_2, 0·8762 = 12·5 per cent. CS_2.

In order to obtain a correct value for the paraffin, the point representing the observed percentage is moved upwards continuously, equidistant from the continuous and then discontinuous straight lines until it reaches the point representing the carbon bisulphide percentage; this point gives the correct value of 3·8 per cent. paraffin.

(2) The mixture taken consisted of: 4 per cent. toluene, 11 per cent. paraffin, 50 per cent. carbon bisulphide, 35 per cent benzene.

Distillation of 100 c.c. to 90° C. yields 97·1 c.c. = 4 per cent. toluene.

As the mixture has a gravity of 1·0496, which is outside the graph, exactly 15 c.c. was diluted five times, *i.e.* to 75 c.c. with pure benzene. The specific gravity of this mixture 0·9150; the specific gravity after removal of CS_2: 0·8794 = 10 per cent. CS_2 = (5 × 10) = 50 per cent. on the original.

The junction of 4 per cent. toluene and the 0·8794 line is at 2·6 per cent. paraffin; this figure corrected as before shows 2·3 per cent. paraffin, which equals (5 × 2·3) = 11·5 per cent. on the original.

It will be realised that for high percentages of carbon bisulphide and paraffin the results will be less accurate than those obtained in the analysis of benzols, but at the same time that there are no serious deviations from the true values.

JONES METHOD.

Based upon the theoretical consideration, that the depression of the freezing point of a liquid, caused by the presence of a dissolved substance, is, in general, proportional to the weight of the solute dissolved in a constant weight of the solvent, F. B. Jones has elaborated the following method of analysis of commercial "pure" benzol.

Application of the Method.—It is evident that a method of analysis such as that described above can be applied to the case of commercial pure benzols. Up to the present time, in order to carry out the complete analysis of a sample of "pure" benzol, it would have been necessary to estimate the carbon bisulphide and the thiophene by gravimetric methods; the toluene by the fractionation of a large bulk of the sample to obtain a residue rich in toluene (the composition of which could be found from its distillation characteristics), and the paraffin either from the consideration of the specific gravity of the sample after the removal of carbon bisulphide and thiophene, or by the removal of aromatic hydrocarbons by exhaustive treatment with sulphuric acid.

The proposed method has the advantage that by its aid an analysis can be completed within one day by the employment of simple operations. By suitable arrangement of the work, this rate is considerably increased when several analyses are carried on together.

The Freezing Point Measurements.—The following provides a means whereby small quantities of carbon bisulphide, thiophene, toluene, and paraffin may be estimated with little trouble, and with a fair approach to accuracy, the measurements required being three freezing points and one specific gravity. The freezing points are determined in the usual way, by means of any thermometer capable of giving readings accurately to 0·01° C. over the range 0–5·5° C. Since, on an average, a difference of 0·01° C. corresponds with about 0·02 per cent. of impurity (0·01 per cent. in the case of carbon bisulphide), this is the theoretical accuracy of the method. Should the best thermometer available be one divided in 0·1° C. readable to 0·05° C., results can be obtained accurately only to 0·1 per cent. (0·05 in the case of carbon bisulphide). In this case, of course, the thermometer corrections must be known to 0·05° C.

The Method of Analysis.—The ice points of the thermometer having been determined, the freezing point (F.P. 1) of the sample is taken. The carbon bisulphide is then completely removed by treatment for not more than one hour with alcoholic potash, avoiding the use of an undue excess of alcohol, followed by three washings with water. The freezing point of the residual benzene free from carbon bisulphide is determined (F.P. 2). The thiophene is then completely removed from the carbon bisulphide-free benzene, according to a method privately communicated by Dr S. P. Schotz, by shaking continuously for 2 to 3 hours with twice its volume of a cold solution of basic mercuric sulphate (Denigès' reagent) prepared by dissolving 5 grams of mercuric oxide in a solution of 20 c.c. of concentrated sulphuric acid in 100 c.c. of distilled water and filtering the solution. The residual benzene is washed twice with cold water in a separating funnel, the water removed, the benzene filtered from suspended solid through a small filter, and its freezing point (F.P. 3) and specific gravity at 15·5°/15·5° C. are determined. The specific gravity must be measured accurately to within 5 in the fifth decimal place, a degree of accuracy obtainable without difficulty if a good type of pyknometer is used, and if the temperature of the bath is known to 0·05° C. In practice it is convenient to take 60–70 c.c. of the sample and remove the carbon bisulphide. The residual liquid is then divided into two portions, 20–30 c.c. being reserved for the determination of F.P. 2. The thiophene is removed from the remaining 40 c.c. It is advisable in all cases to prove the absence of thiophene from the final residue by the isatin and sulphuric acid test.

Employment of the Graph No. 11.—The volume percentage (c.c. per 100 c.c.) of carbon bisulphide is obtained from the graph by reference to F.P. 1 and F.P. 2, the thiophene from F.P. 2 and F.P. 3, and the paraffin and toluene from F.P. 3, and the specific gravity. Theoretically it is necessary to apply corrections to all the values obtained to allow for the increased concentration of the other impurities incident on the removal of carbon bisulphide and of thiophene, but in practice the smallness of the quantities present and the limits of accuracy of the method render this unnecessary.

The Effect of Water.—The material does not need to be dried after the various extractions, for water appears to be sufficiently insoluble in benzene, at temperatures near 5° C., not to affect the freezing point. The liquid of which the specific gravity is to be determined should, however, be dried with a pellet of calcium chloride.

Effect of Other Impurities.—The condition essential to the successful application of the method is that impurities other than the above named shall be either absent altogether or present in not more than the most minute quantity. The sulphuric acid test (90 c.c. of the sample shaken for exactly 5 minutes with 10 c.c. of 90 per cent. sulphuric acid) must not show more than a pure lemon-yellow colour; this indicates that the analysis may be performed directly on the sample as received. Should the acid test show a deeper colour, the sample must be washed for 5 minutes with 5 per cent. of its volume of 90 per cent. sulphuric acid, followed by treatment with caustic soda solution, and several thorough washings with water before proceeding with the analysis. The presence of undesirable impurities is also indicated by the appearance during the treatment with alcoholic potash of a strong yellow colour that appears also in the extracted benzene. Care must be taken that the alcohol used is sufficiently pure, for should it contain aldehydes, coloured resinous substances are produced, and these ultimately contaminate the benzene, which should remain colourless after treatment. For the same reason it is inadvisable to leave the benzene and alcoholic potash in contact for more than an hour. The effect of the impurities in an insufficiently washed sample is to increase the apparent quantity of carbon bisulphide. The thiophene estimation may also be affected to a smaller extent.

Results.—The method has been tested on mixtures of known composition made up from the same materials (with the exception of the benzene) as those used to obtain the figures for drawing the graph.

(1) A known mixture of benzene, carbon bisulphide, thiophene, toluene, and paraffin (the benzene used contained 0·1 per cent. of paraffin).

			Taken	Found.
F pt 1	= 4·43° C.	Carbon bisulphide	0·206	0·21
F pt. 2	4·63° C.	Thiophene	0·499	0·47
F.pt. 3	= 4·84° C.	Toluene	0·129	0·15
Sp. gr.	= 0·8824	Paraffin	1·29 (1·19 + 0·1)	1·3

(2) A known mixture similar to (1), but containing in addition a small quantity of hexylene. The mixture was divided into two portions, one of which was analysed directly, while the other received a preliminary acid washing, as already described. The benzene used contained 0·33 per cent. of paraffin.

	Not Acid Washed	Acid Washed.		Taken	Not Acid Washed	Acid Washed
F.pt. 1	3·95° C.	3·99° C.	Carbon bisulphide	0·367	0·43	0·36
F.pt. 2	4·35° C	4·32° C	Thiophene	0·565	0·46	0·50
F pt. 3	4·56° C.	4·55° C.	Toluene	0·115	0·11	0·12
Sp. gr.	0·88115	0·88115	Paraffin	1·97 (1·61 + 0·33)	2·0	2·0

(3) *Sample of pure benzol.*

Sp. gr.	0·8862	Distillation range (5% to 95%)	0·4° C.
		Sulphuric acid test	— yellow
F.pt. 1	= 5·06° C.	Carbon bisulphide	0·03%
F.pt. 2	= 5·09° C.	Thiophene	0·60%
F.pt. 3	5·37° C	Toluene	0·10%
Sp. gr.	0·8845	Paraffin	0·15%

The method can also be applied in certain cases to well-washed commercial benzols, and for this reason the toluene graph has been extended to 3 per cent.; but in such a case the accuracy of the method is diminished. Should the quantity of toluene exceed about 3 per cent. the method of analysis devised by Spielmann and Wheeler is more widely and more easily applicable.

METHOD OF D. NORTHALL-LAURIE.

Theoretical Considerations.—When a mixture of two chemically similar substances infinitely miscible, such as benzene and toluene, and which do not form a mixture of constant boiling-point, are boiled, the relation between the molecular composition of the vapour and the molecular composition of the mixture is constant, and can be expressed by the equation

$$\frac{X_1}{X_2} = C \frac{W_1}{W_2},$$

where X_1 and X_2 are the relative masses of the constituents in vapour, W_1 and W_2 the relative masses of the constituents in the liquid, and C a constant which is usually a ratio of the vapour pressures.

As the constituent of lower boiling-point boils off, the percentage of the higher boiling-point constituent rises, and so does the boiling-point of the mixture, the composition of the vapour changing in the same manner.

It thus follows that if a mixture of benzene and toluene is distilled at a uniform rate, in a flask, without still head condensation, into an efficient condenser, the composition of the first drop condensed will be equal to the composition of the vapour, and as distillation proceeds, the percentage composition of the distillate will be in inverse ratio to that of the mixture distilling.

If half the mixture is distilled in the above manner, and assuming equal quantities of each constituent present in the mixture, the benzene will be in excess in the fraction distilled, and toluene in excess in the residue.

Again, if the relationship between the percentage composition of the constituents to the boiling-point is known, the amount of each constituent in the fractions can be easily determined.

Mixtures of benzene and toluene, toluene and xylene, of known composition by volume, were prepared, and their boiling-points noted. These were plotted against the percentages and a curve drawn, Graph No. 12, from which the composition by volume for all boiling-points could be read off.

Mixtures of the three homologues will behave under distillation conditions in a similar manner, but in this case the relationship between the percentages of the constituents in the fractions is more complicated. In this case two fractions must be collected. The benzene will then be in excess in the first fraction, the toluene in the second, and the xylene in the residue; there being a proportion of the three homologues in each fraction, this proportion varying according to the percentage composition of the original liquid.

As the three isomers of xylene occur in commercial xylene, and as the percentage of each isomer varies in different samples, slightly varying boiling-points will be obtained in practice. It is found, however, that owing to the boiling-points of the three isomers being so close, namely, 143°, 139°, and 138° C., the error due to taking one fixed boiling-point does not affect the results in any marked degree.

A more complete separation of the mixture into its three constituents would be obtained by using an evaporator still-head and collecting the fractions up to 110·6° C and 139° C., instead of equal amounts. This is, of course, the procedure adopted in fractional distillation.

It is thus seen that plain distillation tends to separate the three constituents, fractional distillation giving a more complete separation.

However, any method of analysis depending on fractional distillation is tedious and likely to be unreliable, unless conducted with great care. Consequently, if sufficient separation of the constituents is obtained by plain distillation in three fractions, so as to give first and last fractions of markedly different boiling-point, a method of determining toluene would be possible.

After a considerable number of experiments the author has devised a practical method depending upon the principles above cited.

Method.—A known volume of the sample is distilled at a uniform rate from a distilling flask into an efficient condenser. As soon as one quarter of the volume has collected, the receiver is changed, and a further half distilled over. The distillation is then stopped. The boiling-points of the first fraction and the last (namely, the residue in the flask) are then taken in an apparatus of special design. On reference to a table or graph prepared as a result of experiment with known mixtures, the quantity of toluene is read off.

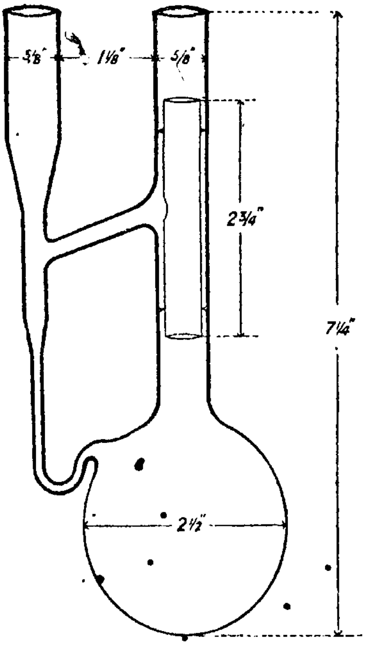

FIG. 54.

This method, depending upon the collection of fractions always of the same quantity and noting the boiling-point, has advantages over the alternative method of collecting fractions to a definite temperature and measuring them, inasmuch as in cases where there is a predominating amount of one constituent the quantity of one or more of the fractions would be small and difficult to measure accurately.

Boiling-Point Apparatus.—The boiling-point apparatus required for us in taking the boiling-point of the fractions is shown in fig. 54.

This can be easily constructed from a distilling flask. In the neck of the flask is placed a thin glass cylinder with a hole in the side corresponding to the outlet of the neck of the flask and sealed to its sides. This glass screen protects the bulb of the thermometer and ensures a steady temperature, preventing variations from draughts or other causes.

Process.—200 c.c. of the sample measured at tap-water temperature are placed in a distilling flask of just sufficient capacity, with the neck cut off close above the side tube. The contents are distilled at the uniform rate of 7 c.c. per minute through an efficient condenser into a 50 c.c. measuring cylinder. When 50 c.c. have collected, the cylinder is quickly changed, without stopping the distillation, for a 100 c.c. cylinder. As soon as 98·5 c.c. have come over, the flame is extinguished and the contents of the flask allowed to cool. By the time that all drops from the condenser have ceased, 100 c.c. will have been collected.

Should the first 50 c.c. be turbid from the presence of water, a pellet of calcium chloride is added, and the cylinder well shaken and allowed to stand.

The contents of the distilling flask are cooled under the tap, transferred to the special boiling-point apparatus, and the boiling-point taken as follows:—

The apparatus is connected to a reflux condenser and boiled at such a speed that the condensed fluid runs back at the uniform rate of one drop per second. The thermometer should be divided into tenths of a degree, and should be tested to ascertain if it is accurate between temperatures of 80° to 140° C. When the temperature has become constant—which takes about 10 minutes—the thermometer is read, the necessary corrections for atmospheric pressure and length of exposed stem made, and the figure noted.

The apparatus is then disconnected, emptied, dried out, and the contents of the 50 c.c. cylinder—which by this time will be quite dry—added. The boiling-point is noted in a similar manner, and on reference to the Graph No. 12 the vertical co-ordinate of which represents the boiling-points of the first fraction, and the horizontal co-ordinate of which represents the boiling-point of the last fraction, the percentage of toluene and benzene present in the sample can be read off. The difference between the sum of these percentages and a hundred represents the xylene.

Advantages of the Process.—There is no need to measure the fractions very accurately, as slight variations in the amounts collected will not affect the value of the boiling-points determined. This obviates the necessity of cooling the fractions to one temperature, which is a source of delay in hot weather.

If the sample is at tap-water temperature, the fractions will necessarily be at the same temperature, thus eliminating any error due to expansion.

The only part of the process requiring special care is in the taking of the boiling-point, which would present no difficulties to a qualified man.

A determination can easily be completed in from 30 to 40 minutes. After the first distillation is finished, the boiling-point of the fractions obtained can be taken whilst the second sample is being distilled; and consequently the process takes no longer than the time required to distil 150 c.c. at the rate of 7 c.c. per minute.

Accuracy.—It will be noted by inspection of the graph that the difference in the boiling-points is quite appreciable for 1 per cent. difference in the toluene present. This difference increases with the increasing percentage of toluene. There is no difficulty in determining the percentages with an accuracy of ·1 per cent.

Limitations of the Process.—The new method will give direct results for all possible combinations of toluene with benzene and xylene in samples containing from 50 to 100 per cent. toluene, the accuracy of the results being greater the higher the percentage of toluene present in the sample. The value of great accuracy in determinations of toluene in commercially pure samples is apparent, it being important to be able to report upon the quality of small impurities in "commercial "pure toluene" now required for the manufacture of tri-nitro-toluene. For samples containing less than 50 per cent. toluene, such as 50s/90s benzols, it would be necessary to add a known quantity of pure toluene so as to bring the results on the graph. This is easily done by taking 100 c.c. of the sample, and 100 c.c. of the toluene, the error produced by doubling the result being more than offset by the greater accuracy of the determination. There is no limitation as to the percentage of benzene or xylene present, so there is no need to add anything but toluene to the sample.

Paraffin.—Any paraffin present in the sample would appear in the analysis as toluene, and the necessary correction must be made for this material. This can be done by the method suggested by Dr Colman, namely, to take in the case of very pure toluene, the gravity of the sample; or in the case of toluenes of lower percentage, the specific gravity of the fractions distilled over between the temperatures of 107° and 115° C., using a Young 12-bulb head.

Every unit in the third place in the specific gravity less than the specific gravity of pure toluene, namely, 0·870, will represent 0·66 per cent. of paraffin in the toluene found.

Example.—The specific gravity of a sample was 0·868. This is two units less than 0·870, 2 × 0·66 equals 1·3 per cent. paraffin. Therefore, if the sample contains 60 per cent. toluene, the paraffin present would be 0·78 per cent.

Carbon Bisulphide.—This material does not occur in toluenes containing over 60 per cent., but is likely to occur in 50s/90s benzols. It is necessary to remove this material before the process can be employed. This is easily done by means of alcoholic potash, the carbon bisulphide being removed as xanthate. The alcohol used must be either pure ethyl alcohol or industrial spirit. Ordinary methylated spirit contains paraffin.

Further Note on Taking the Boiling-Point.—As the whole process depends upon the accurate determination of the boiling-point, care must be taken to always take readings under similar conditions. The apparatus used for this purpose should be of the exact size specified. The flask should be supported 3¼″ above the top of the bunsen burner, which burner must be screened from draughts by means of a cylinder of wire gauze. The flask should rest on a square of asbestos, with a hole 1¼″ in diameter. The stem of the thermometer must be screened from convection currents by means of a square of cardboard slipped over the cork.

An auxiliary thermometer should be suspended within 3″ of the thermometer, so as to give the air temperature immediately surrounding its stem. The whole apparatus should be well protected from draughts.

The rate of boiling must be so regulated that the drops falling back from the reflux condenser do so at the uniform rate of one drop per second.

The most convenient way of regulating this rate is to employ a metronome. With these precautions it is quite easy to obtain rapid observations within one-tenth of a degree.

Boiling-Point Corrections.—It is of course necessary, on account of the changes in atmospheric pressure, to make corrections in the boiling-point. The relationship between the boiling-point of liquids to pressure is expressed by the equation

$$\Delta T = (760 - p)\,(273 + t)\,C,$$

where ΔT is the difference between the observed boiling-point and the boiling-point at 760 mm. pressure, t is the boiling-point of the liquid; p is the atmospheric pressure reduced to 0° C., and C is a constant.

The values of C are:—

For Benzene	0·000121
„ Toluene	0·000120
„ Xylene	0·000115

Within the usual limits encountered, the mean value of this constant can be employed, and the following corrections, which have been determined from the above equation, will apply:—

Pressure.	Correction to be made.	Pressure.	Correction to be made.	Pressure.	Correction to be made.
770	−0·45	759	+0·05	748	+0·55
769	−0·4	758	+0·1	747	+0·6
768	−0·35	757	+0·15	746	+0·65
767	−0·3	756	+0·2	745	+0·7
766	−0·25	755	+0·2	744	+0·75
765	−0·2	754	+0·25	743	+0·8
764	−0·2	753	+0·3	742	+0·85
763	−0·15	752	+0·35	741	+0·9
762	−0·1	751	+0·4	740	+0·9
761	−0·05	750	+0·45	739	+0·95
760	0·0	749	+0·5	738	+1·0

Stem Corrections.—As a portion of the stem of the thermometer has not been entirely surrounded by the vapour of the boiling liquid, another correction is required before the true boiling-point is obtained. The corrections to be added have been calculated from the formula

$$0{\cdot}000143\,(T - t)N$$

when T is the observed boiling-point, t the temperature of the stem outside flask, and N the length of the mercury column in degrees not heated by the vapour.

The following table embodies the values obtained and should be used for the purpose of making the necessary corrections, correction to the nearest 0·05° being taken:—

T – t.

N.	50°	60°	70°	80°	90°	100°	110°
10	0·07	0·09	0·10	0·12	0·13	0·14	0·16
20	0·15	0·17	0·20	0·23	0·26	0·29	0·32
30	0·22	0·26	0·30	0·34	0·39	0·43	0·48
40	0·29	0·35	0·40	0·46	0·52	0·57	0·63
50	0·36	0·43	0·50	0·57	0.65	0·71	0·79
60	0·43	0·52	0·60	0·68	0·78	0·86	0·95
70	0·50	0·60	0·70	0·80	0·91	1·00	1·10
80	0·57	0·69	0·80	0·91	1·03	1·14	1·27
90	0·65	0·77	0·90	1·02	1·17	1·29	1·42
100	0·72	0·86	1·00	1·14	1·30	1·43	1·57

Note on the Graph.—It will be noted that, besides the black line running in a sloping direction and gradually becoming more curved as the percentage of toluene becomes less, there are horizontal red lines running across the graph. These represent percentages of benzene, and the graph, therefore, enables not only the percentage of toluene to be determined, but also the percentage of benzene. The sum of these percentages taken from 100 will give the percentage of xylene.

Conclusion.—The method above described is quick, is applicable to all commercial samples, gives results with an accuracy of 0·1 per cent., and is especially valuable for determining the purity of "pure toluene." It is, of course, only applicable to commercial toluenes that have been washed free from phenols and unsaturated bodies.

THE ESTIMATION OF XYLENE IN SOLVENT NAPHTHA.[1]

METHOD OF SPIELMANN AND JONES.

The difficulty attendant on this estimation is due to the fact that xylene itself consists of three isomers of different boiling points and specific gravities, and that it exists as such in a complex mixture of cumene, tri-methyl-benzenes, and other substances which boil gradually up to 170° C. and over. It has been found that if the benzene, toluene, and xylene be completely removed by careful and repeated fractionation from different makes of solvent naphtha and the fraction of the residue boiling from 143° – 170° C. be examined in a constant boiling point apparatus (such as that devised by Northall-Laurie in connection with his estimation of toluene) the constant boiling point obtained scarcely varies with the different makes.

Commercially pure xylene, fractionated and collected between 138° and 143° C., gives in the same apparatus the constant boiling point of 139·15° C. It becomes possible, therefore, from examination of known mixtures of xylene with the 143° – 170° C. residue, to construct a curve by means of which the composition of unknown similar mixtures may be found from their boiling points.

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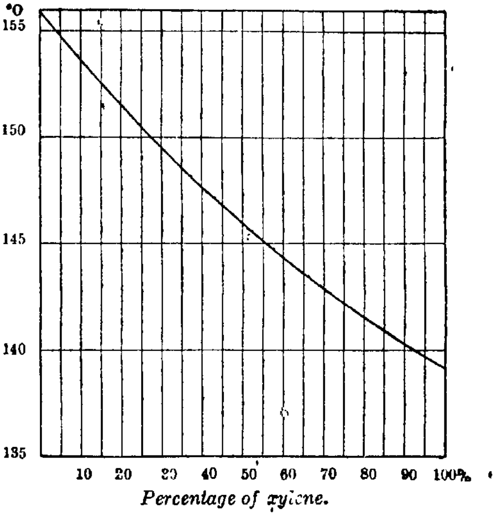
[1] *J.S.C.I.*, 15th May 1917.

100 c.c. (or *200 c.c. if necessary, for Colman's analysis*) of solvent naphtha, accurately measured, is distilled over a Young 12-pear head at the usual rate of one drop a second. The fractions up to 138° C. and from 138° C. – 170° C. (all temperatures being corrected) are collected in separate cylinders and measured.

The benzene, toluene, and xylene in the first fractions (up to 138° C.) are estimated by Colman's methods for examining toluols and solvent naphtha. The xylene in the 138° – 170° C. fraction is evaluated by taking the boiling point in the constant boiling-point apparatus, and referring to graph 13.

All possible care must be taken to get an accurate reading for the boiling point, corrections being made for barometric pressure, thermometer error, and unexposed stem, as is customary in such determinations. A steady temperature is usually attained after about 20 minutes' boiling at such a rate that the liquid condensed from the vapour drops back from the end of the condenser at the uniform rate of one drop a second. After constancy is approximately attained, there is a slow rise in temperature on continued boiling, due, apparently, to the warming up of the unexposed stem of the thermometer, and of the end of the reflux condenser. The accuracy of the boiling point curve may be taken as ± 1½ per cent., when the xylene content of the 143°–170° C. fraction is above 50 per cent., but owing to the divergence of boiling point of the "higher than xylenes" there may be an error of more than ± 2½ per cent. when only small quantities of xylene are present. As, however, the average quantity of xylene in solvent naphtha is about 60 per cent., the region of the curve showing the maximum error will not be employed in practice.



GRAPH 13.

Determination of the composition of mixtures of xylene with the 143° – 170° C. residue from three makes of solvent naphtha other than those from which the curve was constructed :

	Taken (Xylene %).	Found (Xylene %).
1	11·6	14·0
2	29·3	28·8
3	66·9	65·5

For the sake of completeness, a full example is given of the examination of a sample of commercial solvent naphtha, including the corrections for unexposed stem and barometric pressure, and their applications.

The correction for unexposed stem may be obtained from the graph, (page 164).

The correction for barometric pressure is given by the equation :

$$\Delta t = 0{\cdot}046\ (760 - p).$$

Δt is the number of degrees to be added or subtracted according to sign, and p is the corrected barometric pressure (corrected for temperature at the time of experiment).

Example—

Volume from distillation of 100 c.c. over a 12-pear head up to 138° C. = 22·1 c.c.

This 21·1 c.c was mixed with 57·5 c.c. pure toluene and 20·4 c.c. pure benzene, and the mixture analysed by Colman's method. The results indicated that the 22·1 c.c. contained benzene, nil ; toluene, 6·2 c.c. ; xylene (by difference), 15·9 c.c.

Volume from distillation of 100 c.c. over 12-pear head from 138° to 170° C. = 69·7 c.c.

Boiling-point of this fraction :—

Observed reading . . . . . = 141·6° C.
+ thermometer error correction . . 141·7° C.
+ barometric correction (for 755 mm.) . = 141·9° C.
+ unexposed stem correction . . = 143·25° C.

On reference to the curve the fraction is found to contain 67·2 per cent. xylene, corresponding to the corrected boiling point 143·25° C., therefore total content of xylene in the original solvent naphtha $= 15{\cdot}9 + \frac{69{\cdot}7}{100} \times 67{\cdot}2 = 63\ \%$.

Paraffin.—An estimation of the proportion of paraffin associated with xylene may be made by the following procedure, based closely on the method of Wilson and Roberts.[1]

The quantity of the sample—100 c.c. is generally sufficient—is distilled over a Young 12-pear head at the rate of one drop a second, the portion distilling between 138°–143°C. (corrected) being collected separately. 10 to 20 c.c. of this fraction is vigorously shaken for about 40 minutes with 2½ times the volume of weak oleum made by mixing one volume of 22 per cent. oleum with two volumes of 95 per cent. sulphuric acid.

The absorption of the aromatic hydrocarbons is carried out in a 100 c.c. flask, of which the neck is graduated into 10 c.c. and subdivided into 10th's of a c.c. from the volume mark upwards. After sufficient shaking, the level of the liquid is driven up into the graduated neck by the addition of a further quantity of 95 per cent. sulphuric acid.

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[1] *Gas Record*, Chicago ; *J. Gas Lighting*, 1916, 225–227.

After standing—preferably over night—the paraffin will be found to be sharply separated.

Example.—100 c.c. of the solvent naphtha quoted above gave about 23 c.c. between 138° and 143° C., 20 c.c. of this fraction yield 2·5 per cent. of paraffin residue.

This is the quantity present in 20 c.c. of the xylene fraction, therefore, in 63 c.c. of the xylene (*i.e.*, the quantity of xylene found in 100 c.c. of the solvent naphtha) there is $\frac{63}{20} \times 2{\cdot}5 = 8$ per cent. of paraffin.

Therefore this particular sample of solvent naphtha contains 55 per cent. of xylene, together with 8 per cent. of associated paraffin.

ESTIMATION OF THIOPHENE.[1]

Introduction.—The estimation of thiophene in benzene is a problem of importance to certain industries in which benzene is used. It has been found that aniline prepared from benzene containing thiophene resinifies much more readily than aniline prepared from thiophene-free benzene; that the yield of resorcinol is much diminished unless only very little thiophene is present; that much more resin is formed in aluminium chloride condensations if thiophene be present; that thiophene acts in an inhibiting manner in certain other catalytic reactions.

The published information on this matter is so scanty and contradictory that it was considered desirable to examine the methods closely.

METHODS.

Four general methods have been suggested: (*a*) a volumetric method,[2] in which confidence is not aroused, amongst other reasons on account of the varying arbitrary factors to be used; (*b*) a colorimetric method,[3] which might work well if the thiophene present is measured by the blue factor in the tintometer and referred to a previously constructed standard scale; (*c*) gravimetric methods,[4] whereby a precipitate is obtained with either basic mercuric sulphate or acetate (in the latter connection it must be remembered that the boiling toluene reacts with mercuric acetate, acetic acid being set free; but under the conditions of the estimation this reaction apparently does not interfere); (*d*) a method based on the rate of formation of a precipitate under prescribed conditions with basic mercuric sulphate.[5]

Denigès' method—heating the sample in a closed vessel with a solution of basic mercuric sulphate[6]—causes the production of a precipitate not only with thiophene but with many other substances accompanying it—for instance, carbon disulphide,[7] and acetone,[8] using this method obtained a precipitate even with thiophene-free benzene.

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[1] By Percy E. Spielmann, Ph.D., B.Sc., F.I.C., and S. P. Schotz, D.Sc.Tech., B.Sc., F.I.C.

[2] Denigès, *Bull. Soc. chim.* 1896, 862, 1064; *Analyst*, 1896, **21**, 297, 303.

[3] Schwalbe, *Chem. Z.*, 1915, 895.

[4] Cf. Denigès; also of Dimroth (*Ber.*, 1899, **32**, 758); and of Paolini and Silbermann (*Gazz. Chem. Ital.* 1915, **45**, II, 388.)

[5] Denigès, *Bull. Soc. chim.* 1915, **13**, 538.

[6] Denigès, *Bull. Soc. chim.* 1895, **13**, 538.

[7] Denigès, *Bull. Soc chim.*, 1915, **17**, 353.

[8] Schwalbe, *Z. für Farben- und Textil-Industrie*, 1915, **4**, 113.

The use of mercuric acetate under various conditions has been studied by several investigators. Dimroth refluxed 1 kg. benzene (with continued stirring) with a solution of 40 grams of HgO, 300 c.c. H_2O, and 40 c.c. glacial acetic acid for ½ hr. A precipitate of C_4H_4S (HgO.COCH$_3$) HgOH is obtained. Schwalbe[1] examined the addition compound formed and found the sulphur content of the precipitate to be much lower than it should have been according to Dimroth. Applying this method to pure benzene-thiophene mixtures he obtained too high results, *e.g.*, 0·144 per cent. instead of ·1 per cent; 0·662 per cent. instead of ·4 per cent.

Paolini and Silbermann attempted further improvements in this method, which were substantial but insufficient. They boiled a known quantity of the benzene under examination with a slight excess of a solution containing 1 part HgO, 2 parts glacial acetic acid, filtered, and washed the precipitate with ether. Our experience, however, has shown, that the mercuric acetate, which is so obtained, is very sparingly soluble in, and is slightly decomposed by, the commercial ether ordinarily in use; so much so that a blank experiment which was carried out by us according to their instructions with thiophene-free benzene, after very thorough washing indicated ·50 per cent. thiophene. Therefore, according to this mode of working it is necessary to know beforehand closely approximately the quantity of thiophene present in order to work with only a small excess of the precipitating solution, so that subsequent washing with ether should not take an excessive time. In practice when anything up to 2 per cent. (in very rare cases) may be present; a considerable excess of precipitating agent must always be present, so that it is only by chance that the correct proportions would be employed, and only by chance, therefore, that a satisfactory analysis would result.

In the examination of the gravimetric methods, tests were made with thiophene-free benzene to which thiophene (b.p. 84°–84·5° C. (corr.): sp. gr. (15·5° C. 1·0703) was added in known quantities. It should be noted that owing to the large difference between the molecular weights of the reacting substances, which join to form an addition compound, a deviation of 10 mg. in the weight of the precipitate obtained from 10 c.c. of a 1 per cent. solution of thiophene makes a difference of only 0·01 per cent. on the weight of thiophene found.

Denigès' Method.—*Methyl alcohol*, free from acetone, when used as prescribed, gave an immediate yellow precipitate, although Denigès records that such a solution is stable for 5 to 6 hours. Many attempts to find a stable solution failed.

Ethyl Alcohol was tried by us in place of methyl alcohol. In this case, too, a precipitate was formed, and if the proportions of HgO, H_2SO_4, H_2O and alcohol are such that the solution remains clear, it no longer properly dissolves the benzene. However, after the preliminary precipitate was formed, and filtered off, the resulting solution was stable, but for little more than an hour only; this time, however, was sufficient. This modification was found to cause the method to become sufficiently reliable for use as a routine test which has to be carried out quickly, the mode of procedure being the following:—

20 c.c. of Denigès' reagent (5 grams HgO, 20 c.c. concentrated H_2SO_4, 100 c.c. H_2O) are mixed with 60 c.c. of absolute alcohol, shaken well, and filtered. The clear solution is at once mixed with 2 c.c. of the benzole under

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[1] *Ber.*, 1905, 2208.

examination and is allowed to stand for 1 hour with frequent shaking. After filtering through a Gooch filter or tared filter paper the precipitate is washed till neutral to litmus, and dried for an hour at 110–115° C.

The weight of precipitate multiplied by the factor 0·1032 gives the weight of thiophene present in the quantity of sample taken. The composition of the precipitate corresponds to $SO_4\begin{array}{c}\diagup HgO \diagdown \\ \\ \diagdown HgO \diagup\end{array}Hg$, C_4H_4S, so that 1 gram corresponds to $\frac{84\cdot07}{814\cdot272} = \cdot1032$ gram of thiophene. (Denigès gives $\frac{84}{812} = \cdot1034$).

Usually thiophene is present in benzol to an extent of not more than 0·5 per cent., but if more be present an increased quantity of the above reagent must be used. The results tend to be a little high.

Reagent.	Taken Alcohol.	Thiophene.	Found Thiophene.
c.c.	c.c.	%	%
20	60	0·052	0·055
30	90	0·52	0·55
15	45	0·52	0·52
30	90	1·07	0·99 0·91

Many experiments were made varying the proportions of reacting substances, the temperature of their preparation and precipitation, time, and amount of shaking. The examples quoted may be taken as being typical for the best conditions of working, and although the difference shown is as much as 6 per cent. of the quantity of thiophene taken, the practical error is negligible. The method is, however, much more erratic than a method to be described, and requires some practice for successful working; for these reasons it is the less desirable.

Still another modification has been tried, which, however, was not successful. 2 c.c. of benzene was dissolved in 90 c.c. of alcohol, and 30 c.c. of Denigès' reagent was added and the mixture allowed to stand, with frequent shaking, for 1 hour, or longer if thought necessary. Then about 80 c.c. of 20 per cent. sulphuric acid was added, and the mixture was shaken till the yellow colour of the precipitate had disappeared; the residue was filtered off and treated as before. The results were found to be too high, viz. 1·35 per cent. and 1·45 per cent., instead of 1·07 per cent., the deviation apparently resulting from the presence in the alcohol of some reacting bodies, which in the previous mode of procedure were filtered off.

Modified Basic Mercuric Sulphate Method (Recommended).—This method, which gives very consistent results, consists of shaking the sample with an aqueous solution of basic mercuric sulphate in the cold. Under these conditions only thiophene and none of the accompanying substances react. The most important of those likely to interfere is carbon disulphide, and the following figures show that it takes no part in the reaction:—

Thiophene taken	0·0220 gram	= 1·10 per cent.
„ + 5 per cent. CS_2 (on the volume of benzene used).	1·022 grams	= 1·10 per cent.

When testing the method with an approximately 1 per cent. solution of hexylene (probably not quite pure) a trace of a yellow substance, corresponding to less than 0·01 per cent. thiophene was obtained, which suggests that the method may be applicable to crude benzoles.

Mode of Application of the Method.—2 c.c. of the benzole under examination and 20 c.c of Denigès' reagent (see below) are introduced into a strong test tube (about $\frac{7}{8}''$ × 6″) well closed with a sound wet cork and placed in a shaking machine for 3 hours (even without shaking the reaction goes on to some extent). At the end of that time, the white precipitate which is formed is filtered through a weighed Gooch crucible, washed well with hot water till neutral to litmus, dried at 110°–115° and weighed.

The weight of the precipitate multiplied by ·0757 gives the weight of thiophene contained in the 2 c c. of benzole.

The composition of the precipitate has been determined by Denigès, and found to agree with the formula $2(HgO, HgSO_4)\ C_4H_4S$, so that the factor is, in this case $\frac{84\cdot102}{1110\cdot642} = \cdot0757$. (Denigès gives ·0758).

Precautions to be observed:

(1) *Making up the Reagent.*—20 c.c. of pure concentrated H_2SO_4 are poured into 100 c.c. of distilled water and 5 grams finely powdered mercuric oxide added and stirred until almost all has gone into solution. The solution is then filtered, and can be kept in a stoppered bottle for an indefinite time without any signs of decomposition.

(2) The Gooch crucible must be made up afresh for each experiment with good fibrous, specially purified asbestos, on top of which is placed a perforated porcelain plate (Kahlbaum's "pure asbestos" was found unsuitable for this purpose). The prepared crucible must be dried in the same way before and after using.

On shaking for 5 to 6 hours even with only ·02 gram thiophene, the results are very accurate. When shaking is continued only for 1 or 2 hours, the results are slightly lower:

2 hours shaking—taken thiophene: ·02211 gram = 1·10 per cent.
found: ,, 02047 ,, = 1·02 per cent.

The results tend to be low to an extent of about 8 per cent. of the larger quantity of thiophene taken, but here again this discrepancy is of no serious practical matter; it matters little whether 0·48 is found when 0·52 per cent. is actually present; or if 1·00 per cent. is found when 1·10 actually exists.

This method, which has been examined for the optimum conditions of accuracy, had led to the following observations:—

A quarter of an hour vigorous shaking carries the reaction to about 80 per cent. of its course, whilst the next half hour causes it to proceed to over 90 per cent.: at least a full hour, however, is to be recommended.

The employment of larger quantities of the sample and of stronger mercury reagent led to diminished accuracy and a great prolongation of the time necessary for washing, without any sufficient compensating advantages.

The method of *Paolini and Silbermann*, based on the use of basic mercuric acetate in glacial acetic acid—a mixture which is pasty at ordinary temperatures—shows considerably mechanical difficulties which are due mainly to the nature of the precipitate, which is like a dough. The following mode of working, only slightly different from that of the original workers, leads to considerably more trustworthy results.

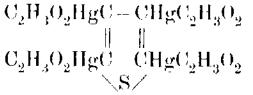
Modified Basic Mercuric Acetate Method (Recommended).—4 grams of Paolini and Silbermann's reagent (previously filtered) are introduced into a suitable test-tube to which 10 c.c. of the benzene under examination are added. The mixture is refluxed in a water bath for about ¼ hour with frequent shaking. When *perfectly cooled* the precipitate is filtered through a Gooch crucible, washed till neutral with water, and dried at 100° C.

The weight of precipitate multiplied by ·07516 gives the weight of the thiophene in the quantity of sample taken.

Examples—

	I.	II.
Thiophene taken	1·06	1·06
„ found	1·01	0·99

The precipitate has a composition agreeing with the formula



$$\begin{array}{c} C_2H_3O_2HgC - CHgC_2H_3O_2 \\ \| \qquad \| \\ C_2H_3O_2HgC \quad CHgC_2H_3O_2 \\ \diagdown S \diagup \end{array}$$

whereby the factor is obtained $\frac{84{\cdot}07}{1118{\cdot}57} = {\cdot}07516$.

A considerable improvement was found in the use of water for washing in the place of ether as prescribed, but even so the washing for a single experiment takes a considerable time.

On the whole the modified mercuric sulphate method is greatly to be preferred, because a stable reagent is being dealt with, there is notable absence of side reactions, it can be carried out successfully without any previous practice, and it is capable of high accuracy.

Further references of value are:—

Denigès' method (gravimetric).

C.r. 1895, **120**, 628, 781, 963. *C.r.* 1908, **126**, 1868. *Bull. Soc. chim.*, 1898, **19**, 754. *Analyst*, 1895, **20**, 188.

Dimroth's method.

Schwalbe, *Ber.* 1905, 2208. Liebermann & Pleus, *Ber.* 1904, **37**, 2461.

ESTIMATION OF CARBON DISULPHIDE.

A CRITICAL EXAMINATION OF THE VARIOUS METHODS USUALLY EMPLOYED.[1]

Lack of sufficient information as to the trustworthiness of the various known methods of estimating carbon disulphide led the authors to examine them with regard to their relative value, the conditions of best results, and the limits of accuracy of each.

The following methods have been examined:—

1. **Solution in Alcoholic KOH,** and elimination of water-insoluble

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[1] Percy E. Spielmann, Ph.D., B.Sc., F.I.C., and F. Butler Jones, B.A., A.I.C.

oils by extraction with water, followed by subsequent treatment according to one of the following methods:—

(A) *Change in Specific Gravity.*—In the case of carbon disulphide being extracted from another liquid such as benzole, estimation can also be made by measurement of the change in specific gravity of the liquid before and after complete removal of the CS_2 by means of alcoholic KOH.

(B) *Oxidation with Bromine.*—The sulphur is oxidised to sulphuric acid, which is then estimated in the ordinary way as barium sulphate.

(C) Acidification of the alkaline solution with acetic acid and estimation of xanthate as cuprous salt either—(*a*) *volumetrically*, by titration with standard $CuSO_4$ solution, using $K_4Fe(CN)_6$ as indicator; or (*b*) *gravimetrically*, by precipitation of cuprous xanthate by excess of $CuSO_4$ solution; the precipitate being either filtered, washed and ignited to CuO; or, again, *volumetrically* by decomposition by bromine or nitric acid, and the copper in solution estimated by a volumetric method.

2. **Precipitation by Phenyl-Hydrazine** of Phenyl-Hydrazine Phenyl-Sulphocarbazide.—(1) The potassium xanthate is ordinarily recommended to be prepared by means of absolute alcohol, but experiments showed that a considerable quantity of water does not inhibit its formation. Pure benzole was freed from CS_2 and its specific gravity determined by means of the specific gravity balance. 0·4 per cent. vol./vol. of CS_2 was then added and the specific gravity of the mixture was determined. Mixtures of alcohol and water were made up containing various percentages of alcohol (estimated by determining the specific gravity), and these were used to prepare alcoholic potash of uniform KOH strength (approximately 10 per cent.). A portion of the benzene-CS_2 mixture was then shaken for 2 hours with (except in one case) half its volume of alcoholic potash. The mixture was then washed five times with water, dried with calcium chloride, and its specific gravity determined. From a knowledge of the specific gravity the quantity of CS_2 removed could be determined. The results are summarised in the following table:—

	Strength of Alcohol per cent by Volume	Ratio Vol. of Benzene / Vol of Alcoholic KOH.	Sp. Gr. Benzene + 0·4 per cent. CS_2.	Sp. Gr. after treatment.	Sp. Gr. free from CS_2.	Per cent. on Total Mixture.
(1)	96·1	2	0·8861	0·8844	0·8844	0·45
(2)	89·6	2	0·8861	0·8845	0·8844	0·4
(3)	85·6	2	0·8861	0·8845	0·8844	0·4
(4)	77·5	2	0·8861	0·8845	0·8844	0·4
(5)	69·6	2	0·8861	0·8846	0·8844	0·4
(6)	49·8	2	0·8862	0·8848	0·8844	0·35
(7)	35·8	2	0·8862	0·8852	0·8844	0·25
(8)	48·8	2	0·8874	0·8861	0·8844	0·35
(9)	6·7	0·5	0·8862	0·8854	0·8844	0·2

Nos. 8 and 9 do not belong to the series 1–7. No. 8 was carried out on a mixture somewhat richer in carbon disulphide in order to ascertain what quantity of the latter substance was removed by alcoholic potash approximately the same in strength as that mentioned in No. 6; otherwise the conditions were exactly the same as in the series 1–7. It is noteworthy that the same quantity of carbon disulphide was removed, leaving of course a greater quantity unabsorbed than in the case of No. 6.

The purpose of No. 9 was to find out whether alcoholic potash made with alcohol as weak as 7 per cent. by vol. would react at all with carbon disulphide. A much larger proportion of the alcoholic solution was therefore taken (2 vols. of alcoholic KOH to 1 vol. of benzene-CS_2 mixture instead of $\frac{1}{2}$: 1), and the actuality of reaction was substantiated. It is seen, therefore, that alcohol as low as 70 per cent. can be used with safety in the proportions recommended, and that alcohol, as weak as even 7 per cent. by volume (when made into 10 per cent. alcoholic KOH) will suffice to remove some CS_2 from benzene, so that the natural conclusion is that if sufficient treatment is given, alcoholic potash made up with almost any strength of alcohol will remove all the CS_2.

Parallel experiments using alcoholic soda showed that its efficiency in removing the carbon bisulphide from admixture with benzene is equal to that of alcoholic potash.

	Per cent. of Alcohol by vol	Sp. gr. before Extraction.	Sp. gr. after Extraction.	Per cent. CS_2 Present.	Per cent. CS_2 Removed.
(1)	96	0·8858	0·8839	0·55	0·55
(2)	92	0·8858	0·8839	0·55	0·55
(3)	86	0·8858	0·8839	0·55	0·55
(4)	79	0·8858	0·8839	0·55	0·55
(5)	71	0·8858	0·8839	0·55	0·55
(6)	49	0·8861	0·8853	0·65	0·20
(7)	33	0·8861	0·8856	0·65	0·15
	Two check experiments using alcoholic *potash* gave :—				
(8)	96	0·8858	0·8839	0·55	0·55
(9)	50	0·8858	0·8848	0·55	0·25

(1A) *Change in Specific Gravity.*—The degree of accuracy depends upon that of the specific gravity measurements. For benzene-carbon disulphide mixtures, if the specific gravities are measured to the fourth decimal place about 0·03 per cent. can be appreciated.

(1B) *Oxidation with Bromine*[1]—It was already known that this method was accurate, and for this reason exhaustive experiments were not made. It was found, however, that two precautions have to be observed: (i.) a good excess of potash must be used in order that plenty of hypobromite may be formed with the bromine and that the latter must also be added in large excess since a certain quantity of ethyl-bromide is formed; (ii.) the mixture with bromine should be allowed to stand for at least an hour at ordinary temperature, otherwise oxidation may be incomplete. The figures given below illustrate the degree of accuracy obtained :—

CS_2 Taken.	CS_2 Found.	
0·231	0·230	
0·081	0·069	Incomplete oxidation due to neglect of conditions (*a*) and (*b*).
0·081	0·080	

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[1] Allen's *Commercial Organic Analysis.* Revised edition, vol. iii. pp. 227–228.

The authors have not fully examined the method of Stavorinus,[1] which consists of oxidising potassium xanthate with hydrogen peroxide. A preliminary examination showed that it offers little advantage over the bromine oxidation method, and has the disadvantage of requiring the neutral hydrogen peroxide, a relatively large quantity of alcohol in the preparation of the sodium hydroxide solution, and the necessity for a blank of all reagents for sulphate.

(1C) *a. Volumetric method.*—The method of titration of the xanthate solution with standard N/10 $CuSO_4$ solution was found to give uncertain results. These were ultimately traced in part to the effect of excess of acetic acid used. With a large excess of acetic acid, the end point was very variable, even when care was taken to exclude extraneous substances such as benzene from the liquid being titrated; whereas when the excess of free acetic acid was but slight, closer results were obtained.

The potassium ferrocyanide, which is usually employed as an external indicator, either in drops on a waxed plate or as a spot on filter paper, can also be used internally. Cuprous xanthate is only slowly decomposed by potassium ferrocyanide, and as the change in the colour of the mixture from yellow to brownish is about as sharp as the change in colour of the drops on a plate, the internal indicator is to be preferred.

The copper standard was calculated assuming the theoretical ratio $Cu : 2CS_2$ for the reaction. (For N/10 $CuSO_4$, 1 c.c. = 0·0076 gram of CS_2.)

Excess of acetic acid.	CS^2.		Per cent error.
	Taken.	Found.	
Very large	·253	·253	nil
" "	·253	·209	− 17·4
" "	·253	·235	− 7·1
Slight	·074	·074	nil
"	·074	·079	+ 6.8
Very large	·128	·133	− 3·9

It will be noticed that whereas the results in two cases are quite good, the majority were unsatisfactory; the correct results are probably to be ascribed to chance. These figures are closely parallel with those obtained by Mr E. G. G. Wheeler of the D.E.S. laboratory, during the working out of a method of analysis of benzoles. Even with the precautions mentioned the method is an undesirable one, both on account of this uncertainty and of the end point not being very sensitive. It is advisable that the end point should be determined by a blank test under working conditions. Possibly, the rate at which the copper solution is added is an important factor. The quantity of acetic acid required to produce slight acidity can be found by titrating a known volume of the xanthate solution with the dilute acetic acid that is to be used for acidification, it being found preferable to employ litmus or phenolphthalein as indicator.

(1C) *b. Gravimetric method.*—As in the case of the titration method it was found that the estimation of copper in the precipitated cuprous xanthate gave quite variable results, and conditions of precipitation could not be found by which good accuracy could be attained. The author's results agree substantially with the observations of E. S. Johnson.[2]

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[1] *J. Gasbeleuchtung*, **49**, 8; *Chem. Zentr.*, 1916, 1, 706.
[2] *Jour. Amer. Chem. Soc.*, xxviii. p. 1209.

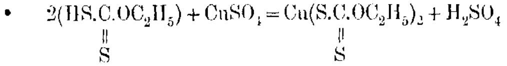
	Excess of Acetic Acid.	Excess of Copper Salt.	Time of Standing	CS_2		Difference.	Per Cent. Error.	Method of Estimation of Copper.
				Taken	Found			
1.	very large	very large	2½ hours	·308	·304	– ·004	– 3·2	Ignition to CuO
2.	,, ,,	,, ,,	1¼ ,,	·138	·120	– ·018	– 13·0	,,
3.	,, ,,	,, ,,	,, ,,	·138	·137	– ·001	– 0·72	,,
4.	,, ,,	,, ,,	4 ,,	·138	·134	– ·004	– 2·9	,,
5.	,, ,,	,, ,,	4 ,,	·138	·134	– ·004	– 2·9	,,
6.	,, ,,	,, ,,	5½ ,,	·138	·133	– ·005	– 3·62	,,
7.	,, ,,	,, ,,	21 ,,	·138	·137	– ·001	– 0·73	,,
8.	,, ,,	,, ,,	28 ,,	·275	·262	·013	– 4·73	,,
9.	large (about half above)	,, ,,	22 ,,	·275	·291	+ ·016	+ 5·82	,,
10.	large (same as 9)	,, ,,	23 ,,	·275	·291	+ ·016	+ 5·82	,,
11.	very large	,, ,,	22½ ,,	·275	·277	+ ·002	+ 0·73	,,
12	,, ,,	,, ,,	23 ,,	·275	·282	+ ·007	+ 2·55	,,
13.	,, ,,	,, ,,	23 ,,	·275	·286	+ ·011	+ 4·00	,,
14.	,, ,, (acid added to mixture of copper solution and Xanthate)	,, ,,	23 ,,	·275	·308	+ ·033	+ 12·00	,,
15.	very large: (Xanthate added to mixture of copper solution and acid)	,, ,,	48½ ,,	·278	·321	+ ·043	+ 15·5	By iodine equivalent with thio.
16.	,, ,,	,, ,,	22 ,,	·278	·299	+ ·021	+ 7·56	By thiocyanic acid equivalent with $KMnO_4$
17.	,, ,,	,, ,,	22 ,,	·278	·304	+ ·026	+ 9·36	,,
18.	,, ,,	,, ,,	20 ,,	·278	·345	+ ·067	+ 22·5	,,
19.	HCl used in large excess with large excess of Na_2SO_3	,, ,,	22 ,,	·278	·315	+ ·037	+ 13·31	,,
20.	very little acetic acid	small	17½ ,,	·081	·082	+ ·001	+ 1·23	,,
21.	,, ,,	,, ,,	18 ,,	·081	·083	+ ·002	+ 2·47	,,
22.	negligible	,, ,,	7 days	·081	·076	– ·005	– 6·15	Ignition to CuO
23.	nil	,, ,,	19 hours	·081	·081	nil	nil	Thiocyanic acid equivalent with $KMnO_4$

Although some of the actual results are apparently very close to the truth it must be remembered that the greatest significance lies in the percentage error, and that if the quantities are aliquot parts which have to be multiplied up, the absolute errors may become considerable. It was observed that rather more accurate results were obtained when the quantity of precipitate was small.

In experiments 1 to 12 a known volume of xanthate was acidified with the acetic acid, and the copper solution added immediately afterwards. It was thought, however, that owing to its great instability the xanthic acid set free might decompose to an appreciable extent before thorough admixture with the copper solution could take place. For this reason in the remainder of the experiments the xanthate was added with stirring to an excess of copper solution and acetic acid already mixed.

It was noticed that when a short time was allowed for precipitation (1 to 6 hours) a further minute quantity of precipitate separated from the filtrate on standing. In every case the mother liquor above the precipitate remained very cloudy for some hours after precipitation, but became clear after about four hours standing, with occasional stirring. The coagulation was hastened by vigorous and prolonged stirring.

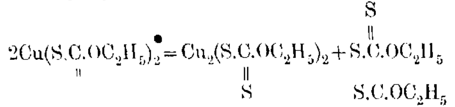
The reaction between copper sulphate and xanthic acid takes place in two stages: (1) the production of cupric xanthate, and (2) the decomposition of this into cuprous xanthate and xanthogen disulphide (dixanthogen):



$$2(HS.\underset{\overset{\|}{S}}{C}.OC_2H_5)+CuSO_4=Cu(S.\underset{\overset{\|}{S}}{C}.OC_2H_5)_2+H_2SO_4$$

Cupric Xanthate.

The cupric xanthate first formed is a brown body, which very quickly decomposes into a bright yellow cuprous xanthate:

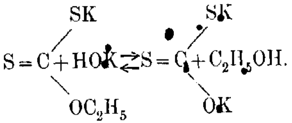


$$2Cu(S.\underset{\|}{C}.OC_2H_5)_2=Cu_2(S.\underset{\overset{\|}{S}}{C}.OC_2H_5)_2+\begin{array}{c}S\\ \|\\ S.C.OC_2H_5\\ S.C.OC_2H_5\\ \|\\ S\end{array}$$

Cuprous Xanthate

Xanthogen Disulphide.

The above results, both volumetric and gravimetric, indicated that the cuprous xanthate was not and could not be obtained pure, the percentage of copper being in most cases too high. A possible explanation is that the xanthate (or ethyl potassium dithio-oxycarbonate) is partially hydrolised in the alkaline aqueous solution during extraction:



$$S=C\begin{array}{l}\diagup SK\\ \diagdown OC_2H_5\end{array}+HOK\rightleftarrows S=C\begin{array}{l}\diagup SK\\ \diagdown OK\end{array}+C_2H_5OH.$$

The dithio-oxycarbonic acid (set free in the presence of acid) would then yield a copper salt containing more copper than the xanthate.

It is unlikely that the high copper content of the precipitate is due in all cases to the adsorption of soluble copper salts, since the results are high even when these are in very slight excess; but it is very probable that the abnormally high results obtained, in some cases, with larger excess of copper solution are at least in part to be ascribed to adsorption.

The suggestion that the high results are due to the formation of CuS or $CuSO_4$ on ignition of the xanthate is contradicted by the fact that high results are also obtained when the copper is estimated volumetrically.

Note.—In order to avoid the possible action of aqueous alkali on the xanthate and also to prevent the escape of xanthic acid from reaction with the acidified copper-sulphate solution, the benzene-alcohol-sodium hydroxide solution was shaken directly with the acidified copper sulphate solution, whereby copper xanthate was immediately formed. This mode of precipitation failed owing to mechanical troubles of collection and filtration of the precipitate in presence of two such liquids as benzene and water.

Detailed experiments were not carried out with the estimation of the residual copper in solution after the precipitation of copper xanthate, as it was found that, whether copper sulphate or acetate were used, the precipitate was not very constant in composition, so that the remaining excess of copper would also be inconstant.

(2) *Precipitation by means of Phenyl-hydrazine.*—This method has nothing to recommend it except as a qualitative test of inferior value. The authors disagree entirely with Bay, whose quantitative method was dependent on the sparing solubility of the precipitated substance in benzene. They found that no quantitative results were possible owing to the fact that the so-called "sparing" solubility is far too high to permit washing with benzene. The solubility in that liquid was repeatedly demonstrated, and after the trial of several other liquids, namely, ether, chloroform, alcohol and light petroleum (the last failing to dissolve, apparently, either the precipitate or phenylhydrazine, and therefore being useless for separating the two), the method was finally abandoned.

The methods of Holland and Phillips[1] and of Goldberg[2] have not been examined, as they depend on heating the material containing carbon disulphide in a sealed tube, in the one case with aqueous ammonia and ferric chloride, and in the other with aqueous or alcoholic ammonia. In both cases the subsequent treatment described is comparatively laborious.

Neither method can be considered as convenient or more accurate than the extraction as xanthate and oxidation of this with bromine.

Experiments were made to ascertain if a better method of analysis could be secured by means of lead xanthate. This salt was precipitated by adding a solution of potassium xanthate to an excess of lead acetate solution containing more than sufficient free acetic acid to neutralise the alkali in the solution of the xanthate added. A pale yellow, finely divided precipitate is produced, coagulating on stirring into very large flocks which break down on standing into much smaller particles.

The liquid clears quickly (in 15 to 20 minutes) if a fair excess of acetic acid is present.

The precipitated substance is mainly $Pb(SCSOC_2H_5)_2$, but it is not quite pure. Since it decomposes slowly at temperatures above about 50° C. and cannot, therefore, be dried quickly, it is not convenient to make the direct weighing of this substance the basis of a method of anal

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[1] *J.S.C.I.*, 1884, 3, 296.

[2] *Z. angew. Chem.*, 1899, 42, 75.

The quantity of lead contained in the crude precipitate from a known amount of xanthate was estimated in two cases by conversion into lead sulphate. In each case the quantity of lead sulphate found was about 4 per cent. lower than that calculated from the quantity of carbon disulphide in the xanthate.

Theoretically 1 gram of lead sulphate is equivalent to 0·5015 gram of carbon disulphide (assuming pure $Pb(SCSOC_2H_5)_2$ to be formed), and this factor was used in calculating the following results:—

Wt. of $PbSO_4$	CS_2. Taken.	CS_2. Found	Per cent. error.
0·2900	·1454	·1511	– 3·8
0·2875	·1442	·1511	– 4·6

It was found that lead xanthate is soluble in certain organic solvents, including benzene, ether, acetone, and carbon disulphide. A quantity of the substance was prepared by precipitation as above and was purified by crystallisation from benzene. It separated from this and from other solvents in long slender needles of pale yellow colour, grouped in star-like forms. A brown residue of impurity remained undissolved by the benzene, but this was not further examined. The crystals were allowed to dry by exposure to air.

The solubility at ordinary temperature of the crystalline substances in benzene, in acetone, and in carbon disulphide was determined.

Solvent.	Temperature.	Solubility (grams per 100 c.c of saturated solution).
Benzene	18·2° C.	·85
Acetone	18·5° C.	·71
Carbon Disulphide	17·5° C.	·38

The percentage of lead in the crystals was determined by dissolving a weighed quantity in nitric acid, evaporating with sulphuric acid to remove all traces of nitric acid, diluting with water, and adding twice the volume of alcohol. The mixture was allowed to stand for 3 to 4 hours, and was then filtered through a Gooch filter, the lead sulphate being well washed with a mixture of alcohol with a little water, ignited and weighed.

The percentage of lead found was 45·6 against the theoretical 46·1, a result sufficiently accurate to prove the composition of the substance to be $Pb(SCSOC_2H_5)_2$.

APPENDIX I.

SOME CONSTITUENTS OF COAL TAR AND THEIR PROPERTIES

("Uber seltenere und Reinpraparate aus Steinkohlteer"—WEGER, *Zeitschrift fur angewandte Chemie*, xxii. 1. pp. 338, 391)

A TRANSLATION
WITH ADDITIONS AND OTHER MODIFICATIONS

BY

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Dr Spielmann has revised the following Appendix since its first appearance, when circulated privately from the D.E.S. of the Ministry of Munitions.

SOME CONSTITUENTS OF COAL TAR AND THEIR PROPERTIES.

The three to four hundred substances which have been found in coal tar —of which only about 150 have been estimated, and only 90 have been definitely isolated—can be divided into a number of classes according to their constitution and behaviour.

These are, broadly, neutral bodies, acid oils, and basic substances. Each of these are characterised by the absence or presence of oxygen, sulphur and nitrogen, which may form part of the aromatic ring, or be attached to it. Further, the fundamental ring may consist of a 6-membered ring, exemplified by benzene, toluene and pyridene, which may be multiplied, giving naphthalene, phenanthrene, truxene, and others; of a 5-membered ring, represented by cyclopentadiene, thiophene, etc., whilst a combination of the two—coumarone, hydrindene, etc.—is to be found. The 4-membered ring is not represented.

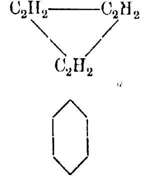
A certain number of less important substances may also be identified, of which many are not of the aromatic class of bodies.

It is remarkable that out of the large number of substances present in tar, only four have been obtained pure on the large scale, namely, benzene, toluene, naphthalene and phenol; whilst of others of which large use is made, the xylenes and cresols are employed in the form of mixtures of their homologues; or a whole series of homologous hydrocarbons may be used, such as those that constitute solvent naphtha, etc.

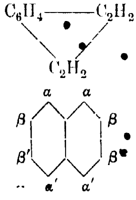
Some of the sulphur, oxygen and nitrogen compounds are left remaining in the particular mixture of hydrocarbons in which they occur, but others have to be removed by further treatment, such as acetone, acetophenone, coumarone, biphenylene oxide, etc.; thiophene, thiotolene, thiocoumarone; nitriles, pyrrole, carbozole, etc.

The isolation of these coal-tar substances on the small scale may be effected by methods used in the works, but in addition to these, the following reactions have been employed: sulphonation and recrystallisation of the sulphonic acids or their salts, followed by decomposition of the acids[1] or their fractional decomposition;[2] precipitation by means of picric acid, and decomposition of the picrates;[3] polymerisation and depolymerisation; and, finally, recrystallisation from benzene, pyridine, alcohol, etc.

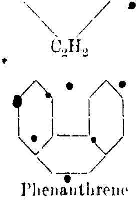
In the following considerations of the *6-membered ring hydrocarbons* the latter are best looked upon as being formed by the union of three C_2H_2 groups, each of which may be replaced by one or more C_6H_4 groups.



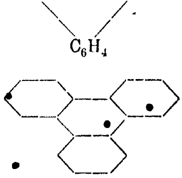
Benzene
C_6H_6



Naphthalene
$C_{10}H_8$



Phenanthrene
$C_{14}H_{10}$



Triphenylene
$C_{18}H_{12}$

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[1] Kelbe, *Ber.*, 19, 92.

[2] Raschig, D.R.P. 114,975.

[3] A.-G. für Teer- und Erdöl-Industrie, D.R.P. 53,792.

The following details should be noted in connection with systematic nomenclature. The termination *-ene* (benzene, toluene, etc.) is reserved for the chemically pure substance; *-ole* (benzole, toluole, etc.) for the commercial product; *-ol* is the German termination for both of the above classes of substances The latter is objectionable as being unnecessary and also in causing confusion, as it is properly reserved for the alco*hol* group (phen*ol*, not phen*ole*).

Benzene—C_6H_6; b.p. 80·3° C.; s.p. 5·48° C.; specific gravity (15·5° C.): 0·885—can be obtained by washing a product, chosen for its purity from paraffin, with a small quantity of strong H_2SO_4 in order to remove thiophene. Complete freedom from paraffin is unusual.

Benzole—The pure benzole of commerce, known as "crystallisable benzole," specific gravity (15·5° C.): 0 884 (average); b.p. 80·3° C (± 0·25)° C. (average); s p. 5° C. (average)—still contains thiophene and carbon disulphide as well as traces of toluene, paraffin, etc.

The quantity of thiophene in benzole, according to V Meyer,[1] reaches 0 5 per cent., "since benzole contains 0 2 per cent of sulphur." This is incorrect, as Meyer apparently took no account of the content of carbon disulphide in benzole, whereby the quantity of thiophene is caused to be estimated much too high, since his method of analysis, by heating six days with fuming nitric acid, causes carbon disulphide to be attacked

The content of thiophene in benzole can be ascertained by titration by Denigès' method,[2] which is based on the peculiarity of thiophene to become added to basic mercuric sulphate; but Dimroth[3] probably obtains more accurate results by employing mercuric acetate, even though Schwalbe,[4] who finds that Denigès' method gives rise to a precipitate even with thiophene-free benzole, states that Dimroth's method also gives too high results. Schwalbe recommends a calorimetric comparison with known mixtures of pure thiophene and pure benzene.[5] The proportion of thiophene in this quality of benzole seldom rises above 0·3 per cent.

Usually only a qualitative test for thiophene is made, by means of the indophenin reaction (isatine and sulphuric acid) and by the Liebermann reaction (concentrated sulphuric acid containing nitrous acid)[6] The first reaction is considerably the sharper.[7]

Thiophene-free benzole is also an article of commerce, and is obtained by thorough washing of the ordinary benzole with sulphuric acid.

The quantity of carbon disulphide present in pure benzole seldom reaches 0·2 per cent. Since the carbon disulphide is known to react with ammonia to form ammonium thiocyanate and ammonium sulphide, and also with alcoholic potash to form potassium xanthate, these reactions can be employed for its removal from the benzole. The last named method can be employed for quantitative estimation by titration with copper sulphate, or by difference in specific gravity found before and after the extraction.[8]

For many purposes, the presence of carbon disulphide is of no importance; but when benzole is used as a solvent during chemical reactions, attention must be given as to whether carbon disulphide will be harmful or not.

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[1] *Ber.*, **16**, 1465.

[2] *Bull. Soc. chim*, **15**, 1064; *Compt. rend*, **120**, 628, 791.

[3] *Ber.*, **32**, 658.

[4] *Chem. Ztg.*, **29**, 895.

[5] See also Spielmann and Schotz, *Jour. Soc. Chem. Ind.*, 1919.

[6] *Ber.*, **16**, 1473; **20**, 3231.

[7] Schwalbe, *Ber.*, **37**, 324; and Liebermann and Pleus, *Ber*, **37**, 2461

[8] See also Spielmann and Butler Jones, *Jour. Soc. Chem. Ind.*, 1919.

Commercially pure benzol is the raw material for the production of mono- and dinitro-benzene, which finds employment as such or after reduction; also of the mono- and di-sulphonic acids, from which phenol and resorcinol are produced synthetically.

90% Benzole.—By far the greater quantity of benzole, however, is not obtained as the commercially pure substance, but as a mixture with about 15–20 per cent. toluole and some xylole. In this form it is employed as a solvent for extractions in the linoleum and varnish industries; in rubber manufacture; for extracting fat from bones; as fuel for stationary and automobile motors; for carburetting coal and water gas; and as a burning material in specially constructed lamps (Denayrouze patent).

"Standard" Benzole, distilling 95 per cent. at 90° C., including not more than 7 c.c. below 80° C., is a quality demanded by the Government under conditions of war. A liquid of this character contains 7 per cent. toluene, and is suitable for the same purposes as the 90's benzole.

Benzole, as well as toluole and xylole, affords an excellent means for the removal of water from other bodies, and is employed in the determination of water in tar, naphthalene, cellulose compounds, butter, sausage, etc., also in the removal of water from alcohol.[1]

Toluene—$C_6H_5CH_3$; b.p. 110·8° C.; f.p. – 92·4° C.; specific gravity (15·5° C.): 0·872—can be obtained from certain makes of toluole, in the same way as benzene from benzole.

Toluole—commercially pure: b.p. 110·8 (± ·25)° C. (average); f.p. – 90° C. (average); specific gravity (15·5° C.): 0·870 (average)—contains traces of benzole, xylole, paraffin and thiotolene. The latter can be identified by the Laubenheimer action, for which the following procedure and proportions are to be recommended:— 3 c.c. of a concentrated solution of phenanthraquinone in glacial acetic acid are poured into a cylinder containing 10 c.c. of the toluole to be tested. 1·5 c.c. of strong sulphuric acid are added, and reaction is continuously brought about by gentle shaking under a stream of cooling water. The formation of a green colour indicates the probable presence of thiotolene. This is confirmed by careful dilution with 3·5 c.c. of water, cooling the while, removal of the top layer and shaking out the lower (acid) layer, with an equal volume or more of ether. The upper ether layer will become coloured like bluish red wine. It is important that no appreciable heating takes place during the reactions of the test.

Toluene is employed in the explosives industry (trinitrotoluene), in the preparation of toluidine, benzyl chloride, benzyldehyde, saccharine, etc., and in the synthesis of indigo. Toluene free from thiotolene is also an industrial product.

Xylene, $C_6H_4.(CH_3)_2$, exists in three isomeric forms: *ortho-*, b.p. 142–143° C.; m.p. – 28 to – 28·5° C.; sp.gr. (15·5° C.): 0·8682; *meta-*, b.p. 139° C.; m.p. –54·8° C.; sp. gr. (15·5° C.): 0·8691; *para-*, b.p. 138·5° C.; m.p. 15° C.; sp. gr. (15·5° C.): 0·8661. The three isomers occur in coal tar in somewhat varying proportions, but the following may be taken as average figures (after the acid washing necessary for purification): 10–16 per cent. orthoxylene, 70–75 per cent. metaxylene, 20–25 per cent. paraxylene.

Xylole—b.p. 138–143° C. (as nearly as possible); sp. gr. (15·5° C.): 0·866 (average)—consists of a mixture of the three isomers containing about 60 per cent. meta-xylene, 10–25 per cent. ortho- and para-xylene, together with ethyl benzene, and smaller quantities of trimethyl benzene, paraffin, and thioxene.

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[1] S. Young D.R.P. 142,502.

Xylole is used in the preparation of nitro-xylene, and is employed in a small quantity for the removal of naphthalene stoppages in gas pipes.

The separation of the three isomers can be effected by the formation of their sulphonic acids, whereby the meta-compound is more easily obtained (and is therefore the cheapest), whilst the ortho-compound is the most difficult to obtain pure. Para-xylene solidifies at +15° C., and can therefore be removed by repeated solidification.

No satisfactory method for the analytical determinations of the three isomers has yet been worked out. An indication of the composition of xylole can be obtained by conversion into a mixture of xylidines of known composition; but this method is troublesome and only applicable in certain cases.

The presence of para-xylole can be ascertained by treatment with small quantities of bromine, whereby para-xylene bromide is precipitated.[1] The method can be made to yield more exact results than those obtained by the authors.

The method of determination based by Levinstein[2] on the fact that meta-xylene is not attacked by dilute nitric acid, and para-xylene is not attacked by concentrated sulphuric acid, is not applicable.[3]

Ethyl Benzene—$C_6H_5.C_2H_5$.; b.p. 135·7° C. (cor.); sp. gr. (15·5° C.): 0·872—was first found in tar xylole to an extent of 10 per cent. by Nolting and Palmer,[4] and was later obtained in larger quantities from the mother-liquor of para-xylene sulphonic acid, by Moschner.[5]

It occurs together with coumarone, phenol, and ethyl phenol during the dry distillation of para-coumarone, when loss of oxygen occurs, and reduction of the coumarone molecule results; it can also be obtained from the distillation products of technical coumarone resin.[6] Para-indene gives no ethyl benzene. Ethyl benzene is characterised by a well crystallising penta-bromide, m.p. 136° C. Ethyl benzene is not present in tar in any great quantity, and is not easily prepared from it, so that this source cannot compete with its synthetic production from bromo-benzene, ethyl bromide and sodium.

Trimethyl Benzenes, $C_6H_3(CH_3)_3$.—All three trimethyl benzenes are present in "tar cumene," and constitute a portion of the solvent naphtha fraction:—

Mesitylene—(1 : 3 : 5), b.p. 164·5° C. (cor.); sp. gr. (15° C.): 0·865—was first identified in tar by Ernst and Fittig,[7] and was first separated directly from it by Jacobsen.[8] This substance, and particularly *Hemellithol*—(1 : 2 : 3 :), b.p. 175° C.; sp. gr. (15° C.): 0·901—are very difficult to prepare. The latter was first isolated 10 years later by Jacobsen.[9]

Pseudocumene—(1 : 2 : 4), b.p. 169·8° C. (cor.); sp. gr. (15° C.): 0·888—also identified in tar for the first time by Ernst and Fittig,[10] and also first separated from it by Jacobsen,[11] is the most abundant of the isomers, and the easiest to obtain pure on account of the sparing solubility of its sulphonic acid in sulphuric acid.

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[1] Radziszewsky and Wispek, *Ber.*, 18, 1280.

[2] *Ber.*, 17, 444.

[3] Reuter, *Ber.*, 17, 2028; 18, 2268, 2274.

[4] *Ber.*, 24, 1955.

[5] *Ber.*, 34, 1261.

[6] Kramer and Spilker, *Ber.*, 33, 2257.

[7] *Liebig's Ann.*, 139, 184.

[8] Jacobsen, *Ber.*, 9, 256.

[9] *Ber.*, 19, 2511.

[10] *Liebig's Ann.*, 139, 184.

[11] *Ber.*, 9, 256.

The majority of the aromatic hydrocarbons boiling from 170–220° C. have not been identified, but the following have been found:—

Cumene (Isopropyl Benzene), $C_6H_5CH(CH_3)_2$, b.p. 152·5–153° C.; sp. gr. (0° C.): 0·8587.[1]

Cymene (1-Methyl 4-Isopropyl Benzene), $CH_3.C_6H_4.CH(CH_3)_2$, b.p. 175° C; sp. gr. (0° C.): 0·8723.

Durene—(1 : 2 : 4 : 5-Tetramethyl Benzene)—$C_6H_2.(CH_3)_4$; m.p. 80–81° C.; b.p. 196° C.[2]—crystallises in white scales and possesses a faint fluorescence.

A use in the pure state for all these hydrocarbons has not been found, except for pseudocumene in small quantities; but in a mixture which contains greater or less quantities of xylene, they constituted two grades of solvent naphtha, that distilling 90 per cent. to 160°, and that distilling 90 per cent. to 175°.

There is an appreciable industrial demand for such a mixture, particularly for chemical cleaning, in the preparation of ordinary varnishes, and in linoleum factories. Further, an addition of 5 to 30 per cent. of it is recommended in burning oil[3]; and more recently, attempts have been made to employ it as an explosive.[4]

Finally, amongst other homologues of benzene the two following substances have been obtained from tar, though with considerable difficulty:—

Phenyl Benzene (Diphenyl), $(C_6H_5)_2$; m.p. 70–71°; b.p. 254° (cor.); sp. gr. 1·165.[5] It crystallises in large colourless scales, and dissolves readily in alcohol and ether.

Venyl Benzene (Styrene), $C_6H_5.CH = CH_2$, still liquid at -20° C.; b.p. 144–145° (cor.); sp. gr. (15° C.): 0·907.[6].

Sulphuric acid causes the formation of molecular compounds with toluene, xylene, etc., which can be distilled without decomposition.

It must be remembered when considering the employment of solvent naphtha, that its smell is of greater importance than the presence of traces of chemical impurities, such as unsaturated hydrocarbons, which might exert a disturbing influence, if, like benzole, it is to be worked up further. It is, however, misleading to judge solvent naphtha by its smell alone without taking into consideration the sulphuric acid test—sulphuric acid test and odour do not go parallel with one another.

These light hydrocarbons are appreciably affected by atmospheric oxygen, which acts by autoxidation slowly or with extraordinary energy, depending on the chemical construction of the substance. Particularly is this so in the case of unsaturated hydrocarbons, such as mono- and di-cyclopentadiene, styrene, and indene, which undergo autoxidation to such an extent that it is very difficult to obtain them in an oxygen-free condition for analysis.

Atmospheric oxygen also affects the partially hydrogenised hydrocarbons, such as hydrindene, hydronaphthalene and the like, to a degree, that all these substances can only be preserved in a sealed glass tube. To a less, but still marked degree, this reaction is also shown by the more completely saturated substances, such as pseudocumene, the xylenes, toluene, and, to a certain extent, even benzene. The changes which all these undergo when standing in air, particularly in the presence of light, are most easily traced by means of the sulphuric acid reaction, which is rendered the worse the further oxidation has proceeded.

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[1] Schultz, Perl and Szeleby, *Ber*., 1909, 3616.
[2] Schulze, *Ber*., 18, 3032.
[3] Plehn, D.R.P. 56,988.
[4] Schultz, English Patent, 19,565; compare *Chem. Ztg. Rep*., 1908, 254.
[5] Buchner, *Ber*., 8, 22; and others.
[6] Berthelot, *Ann. Chim*., 1867, suppl. 5, 367.

It has been shown[1] that in certain cases, 10 per cent. of oxygen may be absorbed, accompanied by the formation of acids which can be extracted. For example, benzoic acid has been isolated from toluene; whilst from para-xylene there has been obtained pure toluic acid, identified by its melting point, 176° C., and by analysis (found: carbon, 70·6 per cent.; hydrogen, 5·81 per cent.—calculated: carbon, 70·59 per cent.; hydrogen, 5·88 per cent.)

If ozone be passed through benzene, the escaping vapours are strongly acid.[2]

The *multiple 6-ring hydrocarbons* with and without external groups uniting two or more rings, constitute a most important class.

Naphthalene—$C_{10}H_8$, s.p. 79·6–79·8° C.; b.p. 218° C.; specific gravity (15° C.): 1·1517 (comp. H_2O at 0° C.)—is peculiar in its high volatility and its capacity for dissolving large quantities of air when molten, which are given up on solidification.

As put upon the market, it is almost chemically pure, and for special purposes it can be prepared absolutely free from traces of phenol. Its estimation can be made by means of its picrate.[3]

Naphthalene is employed for the preparation of phthalic acid,[4] by heating naphthalene—as well as phenanthrene or anthracene—with sulphuric acid at 200° C., with or without the addition of metallic compounds, particularly mercury; it is also employed in the preparation of nitro-naphthalene, naphthylamine, naphthalene sulphonic acid and naphthol, as well as their derivatives, such as zinc naphthalene sulphonate,[5] and magnesium naphthalene sulphonate,[6] which are employed for the preservation of wood.

Formaldehyde and methylal react with naphthalene, forming dinaphthyl methane.[7] More recently this reaction has been taken up for the preparation of artificial gums.[8] Unfortunately these gums are not soluble in spirit, and therefore cannot completely take the place of shellac.

The dye and chemical industries only take up a portion of naphthalene obtained, so that other means of utilisation have to be searched for, such as the substitution for pitch in the production of briquettes[9] for extraction purposes, as in the case of waxes and asphalt, in the place of benzole and the like,[10] and particularly as motor fuel.

Unlike naphthalene, the two **Methyl Naphthalenes**—$C_{10}H_7(CH_3)$, α-, m.p. -22° C., b.p. 241–242° C.; specific gravity (19° C.): 1·005; β-, m.p. 32·5° C.; b.p. 241–242° C.—are very expensive materials. The α-compound is a colourless oil, possessing a high refractive index and a marked fluorescence. The β-compound somewhat resembles naphthalene in appearance. They were first prepared from tar in the crude state by Schulze,[11] who obtained β-methyl naphthalene by fractionating tar oil boiling 239–242° C. (which had previously been freed from acid and alkaline compounds), freezing it, filtering on a suction pump at 0° C., and recrystallising the solid portion from alcohol; whilst the α-methyl naphthalene was prepared by the further cooling to −115° C. of the liquid portion from the above filtrate, and the removal of the crystals of the β-compound.

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[1] Weger, *Ber.*, **36**, 309.

[2] Houzeau and Renard, *Compt. rend.* **76**, 572; *Liebig's Ann.* **170**, 123; Leeds, *Ber.*, **16**, 975.

[3] Knublauch, *Jour. Gasbeleuchtung*, 1910, **61**, 134, 145; *Jour. Soc. Chem. Ind.*, 1918, **37**, n. 58A.

[4] Bad. Anilin- und Soda-Fabrik, D.R.P. 91,202.

[5] D.R.P. 118,101.

[6] D.R.P. 150,110.

[7] Grabowsky, *Ber.*, **7**, 1605.

[8] English patent 16,245, of the Bad. Anilin- und Soda-Fabrik; *Chem. Ztg. Rep.*, 1908, 325; D.R.P. Anm. of the same works, B. 46,200, Kl. 12·0.

[9] Buss and Fohr, D.R.P. 186,396.

[10] Kohler, D.R.P. 204,256.

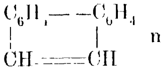
[11] *Ber.*, **17**, 842.

A fluid methyl naphthalene had previously been obtained from tar oil by Reingruber[1] but according to its chemical behaviour it was neither the α- nor the β-compound.

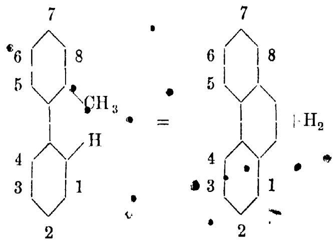
Creosote oil of commerce distilling mainly 200–300° C contains about 6 per cent. of these substances.

Dimethyl Naphthalenes, $C_{10}H_6(CH_3)_2$, were detected in coal tar by Emmert and Reingruber[2] and can be obtained from the fraction boiling 260°–265° C., or from the solid hydrocarbon mixtures which can be separated from this, by sulphonation of the material and subsequent decomposition of the sulphonic acids.[3]

1 : 6—*Dimethyl Naphthalene*, b.p. 265° C., is an oil of faint odour.
2 : 6— „ „ m.p. 109–110° C ; b p. 260°–261° C. ; and
2 : 7— „ „ m.p. 96–97° C. ; b.p. 262° C., both crystallise in leaflets.

Phenanthrene - 
$\begin{array}{l} C_6H_4 - - C_6H_4 \\ | \qquad\qquad | \\ CH = = CH \end{array}$
m.p. 96° C. ; b p. 340° C. (cor.),—is present in coal tar in considerable quantity. It is easily soluble in benzene hydrocarbons (and carbon disulphide), and by this means can be separated from anthracene and carbazole which boil at the same temperature; from the latter it can be separated by fusion of alkali, which with carbozole forms a compound, but not phenanthrene. In order to remove the last quantities of anthracene—about 3 per cent. which cannot be separated by re-solution—other methods have to be employed, whereby the pure product is put upon the market containing less than ½ per cent. of anthracene. Oxidation yields the characteristic phenanthraquinone. Estimation, see Hildebrand, Ellesson, and Beche.[4]

It is formed pyrogenetically from 9-ethyl or 9-methyl fluorene[5] according to the formulæ:—



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[1] *Liebig's Ann.*, 206, 375. [2] *Ibid.*, 211, 365.
[3] Ges. fur Teerverwertung; D.R.P. 30,1079, 1916.
[4] *Jour. Chem. Soc.*, 1917, **39**, 2301; *Ibid.*, 1918, Abstract i., 62.
[5] Græbe, *Ber.*, **37**, 4145.

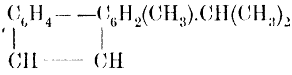
and by many other pyrogenic reactions. Interesting and typical is that of Kramer and Spilker[1] from coumarone and benzene:

$$C_8H_8O + C_6H_6 = C_{14}H_{10} + H_2O + H_2.$$

It consists of colourless scales, when crystallised from alcohol, showing a faint blue fluorescence.

Phenanthrene and its derivatives have been employed in the dyeworks to only a limited extent, but it is not impossible that demand will increase, as the opium alkaloids (morphine, codeine, thebaine) are phenanthrene derivatives. Attempts have been made to utilise phenanthrene by its addition to gum resin[2] and as an addition to paraffin.[3]

Retene, (5-Isopropyl 8-Methyl Phenanthrene)—



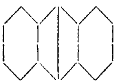
$$\begin{array}{l} C_6H_4 - -C_6H_2(CH_3).CH(CH_3)_2 \\ \;| \qquad\quad\; | \\ CH - CH \end{array}$$

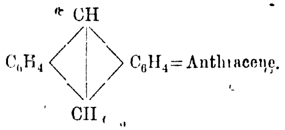
s.p. 90-95° C.; m p. 98-99° C.; b.p. 350° C.—found in coal tar by Kraus[4] and in wood tar.[5] It forms shining scales of no odour, and volatilises slightly at ordinary temperatures. At red heat, it yields a considerable quantity of anthracene.

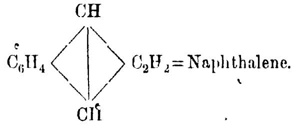
The last member of this series is **Triphenylene**, $C_{18}H_{12}$, which has not yet been identified in coal tar, but is certainly present in it.

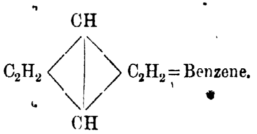
It occurs as a by-product in the preparation of diphenyl from bromobenzene and sodium; also by heating benzene to a high temperature[6]; finally from dodekahydrotriphenylene, by distillation with zinc dust, or over copper (Sabatier): the substance results from the condensation of three molecules of cyclohexanone.[7]

Another series of which we only know the highest member (since the lowest are so labile that they immediately change into naphthalene and benzene) is anthracene.









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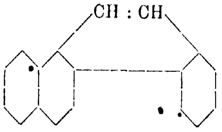
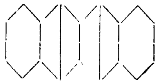
[1] *Ber.* **23**, 85.
[2] Drehe, D.R.P. 113,233.
[3] Lewy, D.R.P. Anm. L., **24**,443.
[4] *Ann. Chem. Pharm.*, **106**, 391.
[5] Ekstrand, *Liebig's Ann.*, **185**, 75.
[6] "Isochrysene" of Schmidt and Schultz, *Liebig's Ann.*, **203**, 135.
[7] Mannich, *Ber.*, **40**, 153 and 159.

The comparison of these three structural formulæ is instructive, but it is unusual to represent benzene in the form of a bridged ring.

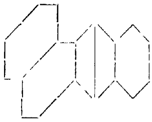
Compare also:



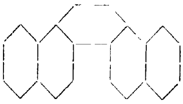
Chrysene.



Naphthacene.

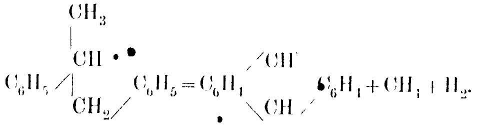


Naphthanthracene.



Picene

Anthracene—$C_{14}H_{10}$, m.p. 213° C.; b.p. 360° C.—was first found in coal tar by Fritzche in 1857. It is formed pyrogenetically from a large number of very different substances, such as toluene, benzene, styrene, turpentine oil, petroleum and others. Of particular interest is its synthesis from toluene-styrene (phenyl toluyl ethane) by Kramer and Spilker:[1]



$$C_6H_5\diagup\left|\begin{array}{l}CH_3\\ |\\ CH\\ \\ CH_2\end{array}\right.\diagup \quad C_6H_5=C_6H_4\begin{array}{l}\diagup CH\\ \\ \diagdown CH\end{array}\diagup C_6H_4+CH_4+H_2.$$

Anthracene dissolves with difficulty in almost all solvents—for instance, in benzene 1·86 per cent., in carbon bisulphide 2·58 per cent., in hexane 0·57 per cent. In the pure state, it consists of flakes showing a blue-violet fluorescence. Its picrate, $C_{14}H_{10}.C_6H_2(NO_2)_3OH$, m.p. 170°, is easily decomposed by alcohol, water, and sodium hydroxide solution.

In the sunlight a solution of anthracene is converted into *para-anthracene* $(C_{14}H_{10})_2$, m.p. given variously as 224°, 244°, 272°–274° C.,[2] which is still less soluble than anthracene. According to Luthe and Weigert,[3] anthracene is converted by sunlight, both in solution and also in the solid state, into

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[1] *Ber.*, **23**, 3269.

[2] Graeber and Liebermann, *Liebig's Ann.*, 1870, Suppl. 7, 264.

[3] *Chem. Zentralb.*, 1904, **2**, 117; 1905, **1**, 1152.

dianthracene, which, in the dark, changes back into anthracene. Chromic acid oxidises anthracene to the very characterirtic anthraquinone. This reaction can be employed for quantitive determination, and is one of the most exact that exist in organic chemistry. The method as described by Luck is the most applicable.

Anthracene, however obtained, is seldom more than 30 per cent. pure, and its purification can be carried out in a number of ways, all of which are based primarily on the removal of carbozole. Crude anthracene is washed with pyridine, quinoline, or aniline bases in which carbozole is more easily soluble than anthracene; also mixtures of the above mentioned bases with benzole can be employed.[1] In this way a substance of 80 per cent. purity can be obtained. Oleic acid for the same purpose had previously been proposed[2] also liquid sulphurous acid,[3] and acetone, methyl-ethyl-ketone or acetone oil[4]

The separation of anthracene from carbozole by distillation from potassium hydroxide has long been known, but is accompanied by much loss. Distillation over potassium hydroxide in vacuo and reception of the distillate into basic substances diminishes this loss,[5] this can also be diminished by melting crude anthracene, and leaving it to crystallise partially; then melting it with potassium hydroxide at 260°, at which temperature a double layer is formed, consisting of the potassium hydroxide-carbozole compound and the hydrocarbon; finally, phenanthrene is removed by benzene.[6] In this way 85–95 per cent anthracene can be obtained.

Carbozole can be separated by conversion into nitroso-carbozole by means of nitrous acid, which is soluble in benzene,[7] or by treating a solution of anthracene with concentrated sulphuric acid which combines with the carbozole.[8]

To obtain a perfectly pure anthracene, further crystallisations must in all cases be carried out. Its most important use is in the production of alizarine.

β **Methyl Anthracene,** m.p 207° (cor.), occurs in tar,[9] but can much more conveniently be obtained from xylene-styrene, by the synthesis of Kramer and Spilker.[10]

Xylene Styrene (Benzyl Xylyl Ethane, or α β-toluyl phenyl propane) —$CH_3.CH(C_6H_5).CH_2C_6H_4CH_3$; b.p. 300° C. with slight decomposition; sp. gr. 0 987—is formed in appreciable quantities from coal-tar xylole and styrene (which boils at the same temperature) under the condensing influence of concentrated sulphuric acid during the washing of crude xylole. It consists of a somewhat thick oil, α β-Phenyl ortho-toluyl propane, prepared from pure ortho-xylene and styrene, boils at 316-317° (cor.); the meta-compound at 311–312° C. (cor); and the para-compound at 302–303° C. (cor). When the vapours of these substances are superheated, methane and hydrogen are split off and mono-methyl anthracene is formed.

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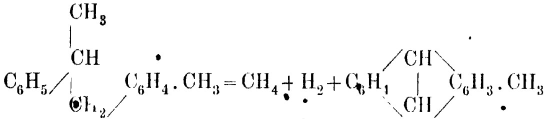
[1] A.-G. fur Teer- und Erdol Industrie, D.R P. 42,093.
[2] Remy and Erhart, D.R P. 38,417.
[3] Farbenfabriken, vormals, Fr Bayer & Co., D.R.P. 68,474.
[4] D.R P. 78,861
[5] D.R P. 178 764 of the A.-G fur Anilinfabrikation.
[6] A.-G. fur Teer- und Erdol-Industrie, D.R.P. 111,359.
[7] Wirth, D.R.P. 122,582
[8] Vesely and Vostock, D.R.P. 164,508.
[9] Japp and Schultz, *Ber.*, 10, 1049.
[10] *Ber.*, 23, 3270.

The ortho-compound gives 1-methyl anthracene and the meta- and para-compounds 2-methyl anthracene according to the formula:



$$C_6H_5\diagup\overset{\overset{CH_3}{|}}{CH}\underset{CH_2\diagup}{|}C_6H_4.CH_3 = CH_4 + H_2 + C_6H_4\begin{matrix}\diagup CH\diagdown\\ |\\ \diagdown CH\diagup\end{matrix}C_6H_3.CH_3$$

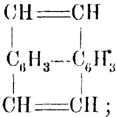
It is obtained from hot alcohol in the form of very bright light yellow needles; and by sublimation, of greenish scales. It is easily soluble in benzene, carbon bisulphide, and chloroform.

Iso-Methyl-Anthracene has been obtained by Bornstein[1] from a non-bituminous Westphalian coal tar. It shows a violet-blue fluorescence in ordinary organic solvents. It is obtained during the reaction of formaldehyde and toluene.[2]

Dimethyl Anthracenes, $C_{14}H_8(CH_3)_2$, have not yet been identified in tar, but are certainly present in it. They can be obtained from pseudo-cumene styrene (phenyl xylyl propane) by a synthesis similar to that described above.

A combination of more than three 6-membered rings gives rise to chrysene, pyrene, naphthacene, naphthanthracene, and picene. On account of the high boiling point of these substances they are not obtained during the ordinary tar distillation, but form a proportion of the considerable number of substances, still quite unknown, which constitute pitch.

Pyrene—

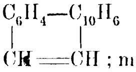


$$\begin{matrix}CH=\!=CH\\ |\quad\quad|\\ C_6H_3-C_6H_3\\ |\quad\quad|\\ CH=\!=CH\end{matrix}$$

; m.p. 148° C.; b.p. far above 360° C.—was found together with chrysene by Graebe.[3] It is obtained by extracting pitch-distillates with carbon bisulphide, evaporating, dissolving the residue in alcohol, and precipitating as picrate, which is recrystallised several times and decomposed with ammonia.

It forms colourless tablets, which dissolve easily in the ordinary solvents.

Chrysene—



$$\begin{matrix}C_6H_4-C_{10}H_6\\ |\quad\quad|\\ CH=\!=CH\end{matrix}$$

; m.p. 250° C.; b.p 430° C.—was first found in coal tar by Laurent.[4] It is the only one of these substances of which the preparation in considerable quantities is not too difficult. It can be obtained from the residue after the carbon disulphide extraction in the preparation of pyrene; but it is better produced not directly from tar, but by synthesis from simpler constituents of tar. When pure, it is quite white.

According to Kramer and Spilker[5] chrysene is formed when the vapours of a mixture of coumarone and naphthalene are passed through a red-hot pipe, according to the formula $C_8H_6O + C_{10}H_8 = C_{18}H_{12} + H_2O$. Also, when the vapours of indene are superheated, hydrogen splits off and chrysene is formed.[6]

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[1] *Ber.*, 39, 1258.

[2] Gross, *J. prakt. Chem.*, 1910, 82, 231.

[3] *Liebig's Ann.*, 158, 285.

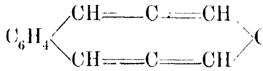
[4] *Annales de Chim.*, 66.

[5] *Ber.*, 23, 84

[6] Kramer and Spilker, *Ber.*, 26, 1544.

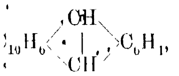
It is best prepared by superheating the vapours of certain high boiling bodies from the heavy naphtha fraction in an iron tube at low red heat.[1]

Naphthacene,



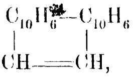
$C_6H_4<\begin{matrix}CH=\!=C=\!=CH\\CH=\!=C=\!=CH\end{matrix}>C_6H_4$, m.p. 335° C., and

Naphthanthracene,



$C_{10}H_6<\begin{matrix}CH\\|\\CH\end{matrix}>C_6H_4$, m.p. 141° C., are both certainly present in coal tar pitch, but have not been isolated.

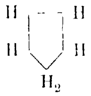
Picene—(*ββ*-Dinaphthylene Ethylene)



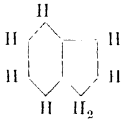
$\begin{matrix}C_{10}H_6-C_{10}H_6\\|\qquad|\\CH=\!=CH,\end{matrix}$

m p. 364° C. ; b p. 518–520° C.—has so far only been found in brown coal pitch and petroleum pitch, but very probably occurs in the heaviest coal-tar oils. It is even less soluble than chrysene.

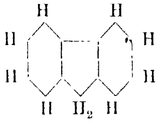
A much more interesting set of substances are the derivative of the 5 *membered ring*, either by itself, or united to the 6-*membered ring*. This group includes cyclopentadiene, indene and fluorene:



Cyclopentadiene
C_5H_6



Indene
C_9H_8



Fluorene
$C_{13}H_{10}$

The members of this class are exceedingly reactive, partly because it contains the atomic grouping

$$—C=C-CH_2-C=C—$$

consisting of a methylene group of feeble acid nature,[2] and apparently also because, at any rate in the first two members, the double bond is external to the benzene ring, and is therefore capable of forming a variety of additional compounds and polymers with ease.

In cyclopentadiene this activity is developed to the highest degree, and the compound therefore is by far the most interesting of all.

Cyclopentadiëne—C_5H_6, b.p 41 °C ; sp. gr. (15°C.): 0·815—is a liquid of characteristic odour. Kramer and Spilker discovered it in 1896 in crude benzole forerunnings, and established its constitution.[3] Almost simultaneously Etard and Lambart[4] described a "pyropentylene," C_5H_6, as a product from the compression of oil gas, without enquiry into its constitution. Probably Roscoe in 1876[5] handled this body in the condition of its simplest polymerisation product, $C_{10}H_{12}$.

Cyclopentadiene is present in varying quantities in benzole forerunnings and oil gas condensate, which is not surprising considering its low boiling point and chemical constitution.

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[1] Klotz, *Ber.*, 23, 84.

[2] Compare Thiele, *Ber.*, 33, 666

[3] *Ber.*, 29, 552.

[4] *Compt. rend.*, 112, 945.

[5] *Liebig's Ann.*, 232, 348.

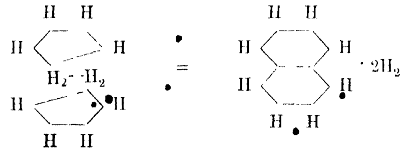
Although its faculty for polymerisation may cause its preparation to appear very simple, in practice there occur various difficulties. Benzole forerunnings contain other substances which have been little studied, having quite similar properties to those of cyclopentadiene, and which also tend to polymerise.

Dilute acids and alkalis resinify these hydrocarbons, and concentrated acids react with explosive violence; chlorine, bromine, hydrochloric acid, hydrobromic acid are added in successive quantities; ammoniacal silver solution deposits a silver mirror. On account of the sensitiveness of cyclopentadiene towards alkalis and acids, it cannot be reduced by ordinary methods to cyclopentane, but this change is easily brought about by the method of Sabatier and Senderens.[1] Atmospheric oxygen attacks it strongly.[2]

The methylene group in cyclopentadiene reacts with ethyl nitrate, oxalic ester aldehydes, ketones, and with potassium, as has been shown by the very remarkable work of Thiele.[3] It also combines with quinones.[4]

Of special note are the beautiful and intensely coloured hydrocarbons named by Thiele, *fulvenes*. They are derived from cyclopentadiene in which the two labile hydrocarbon atoms are replaced by the methylene group (fulvene = $C_5H_4 : CH_2$). Their most characteristic representative is the dark red diphenyl fulvene, which shows extraordinary power of crystallisation.

There remains, lastly, an attempt at a pyrogenic synthesis, not previously published; which is interesting as being an example of a change from a 5-member ring to a 6-member ring. On passing a low molecular cyclopentadiene hydrocarbon, corresponding to truxene, through a tube heated to a low red heat, there was formed an inflammable gas of low luminosity, consisting of hydrogen, and a substance possessing the sought for molecular constitution $C_5H_4 : C_5H_4$, but which was proved to consist of naphthalene by its smell, its melting point at 79·5°, and the melting point of its picrate, 149°.



The yield was a good one; as by-products, benzene and anthracene, were identified. Dicyclopentadiene gave the same results.

On standing, monocyclopentadiene changes spontaneously very easily into **Dicyclopentadiëne**—$C_{10}H_{12}$; s.p. 32·5° C.; b.p. 170° C.; specific gravity 0·977—a colourless crystalline mass, possessing a peculiar smell resembling camphor. It remains indefinitely unchanged in a well-closed vessel. Cyclopentadiene, therefore, can only be preserved in its dimeric form, to be regenerated as required by depolymerisation by prolonged heating under a column.

Dicyclopentadiene is particularly sensitive to oxygen; if air reaches the substance within a short time small reddish-brown globules separate which consist of a hard brittle resin of high oxygen content. Chlorine, bromine and sulphuric acid actively attack dicyclopentadiene. With amyl nitrite and hydrochloric acid, it forms a nitroso-chloride which reacts with organic bases —particularly smoothly with piperidine—like the nitrosochlorides of terpenes. When nitrous acid is passed through a chloroform solution of it, a nitrosate is formed.[1] The formula of dicyclopentadiene must be represented by

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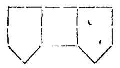
[1] Compare Eijkman, *Chem. Weekblad*, 1903, No. 1.

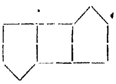
[2] Engler, Autoxidation, *Ber.*, 34, 2938.

[3] *Ber.*, 33, 666; *Liebig's Ann.* 1, 348; *Ber.*, 34, 68.

[4] Albrecht, *Liebig's Ann.*, 348, 31.



or,



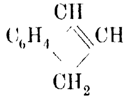
each of which can exist in the cis-trans form; till now, however, it is known in only one modification. Other structural formulæ have been ascribed to it, but without the support of proof.[2]

Dicyclopentadiene is not reduced with sodium, but when passed in vapour form with hydrogen over nickel, tetrahydro-cyclopentadiene (1 : 5, 6 : 10, 1 : 10-*Tricyclodecane*, $C_{10}H_{16}$, is formed, which is a tricyclic terpene, m.p. 77° C.; b.p. 193 °C. This substance possesses a decided odour of camphor, which it resembles in other ways. It can easily be converted by weakly fuming sulphuric acid into an *isomer*, b.p. 191·5° C. (cis- and trans-form).[3]

Kronstein[4] has a short note on the formation of a highly polymerised product of mono- or di-cyclopentadiene, but without mention of melting point or molecular weight.

There exists a large number of polycyclopentadienes of very varying properties, of which a whole series have been prepared.[5]

Indene—



$C_6H_4\left<\begin{array}{c}CH\\ \\ CH_2\end{array}\right>CH$; s.p. -2° C.; b.p. 182·2-182·4° C. (cor.); specific gravity (15° C.): 1·008—was discovered in coal tar by Kramer and Spilken[6]

It is present to an extent of about 20 per cent. of the fraction boiling about 180° C., but is not easily prepared in the pure state. It can be obtained by precipitation with picric acid, but there is difficulty in removing the last traces of coumarone, which is only achieved by fractional distillation. Further, there is the great and disturbing tendency to oxidation and polymerisation.[7] Like cyclopentadiene, indene is very reactive, chlorine, bromine, N_2O_3, etc, being added at the double bond. It gives a nitrosite which on warming changes into nitro-indene.[8] The acid-like methylene group which it contains, leads to the formation of a sodium compound,[9] to its coupling with oxalic ester,[10] and to its condensation with benzaldehyde.[11]

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[1] Kramer and Spilker, *Ber.*, **29**, 559; Weiland, *Liebig's Ann.* **360**, 300.

[2] Weiland, *Ber.*, **39**, 1492.

[3] Eijkmann, *Chem. Weekblad*, 1903, No. 1.

[4] *Ber.*, **35**, 4150.

[5] Weger.

[6] *Ber.*, **23**, 3276. See also Spilker and Dombrowsky, *Ber.*, **42**, 573.

[7] Weger and Billman, *Ber.*, 1903, 640.

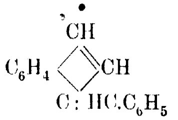
[8] Dennstedt and Ahrens, *Ber.*, **28**, 1331; Wallach, *Liebig's Ann.*, **2**, 336.

[9] Gesellschaft fur Teerverwertung, D.R.P. 205,465

[10] Thiele, *Liebig's Ann.*, **347**, 1275; *Ber.*, **33**, 851; Wislicenus, *Ber.*, **33**, 771.

[11] Thiele, *Liebig's Ann.*, **347**, 249; *Ber.*, **33**, 3395.

With one molecule of benzaldehyde there is formed *Benzylidine indene*,



$$C_6H_4\langle CH \rangle CH, \; C:HC.C_6H_5$$

m.p. 88° C.; with two molecules, *Hydroxybenzyl benzylidene indene*, m.p. 135° C. According to the Thiele scheme of nomenclature, both of these are fulvenes and are indeed coloured an intense yellow, but unfortunately fulvene cannot be regenerated out of either of these compounds.

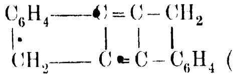
This condensation with benzaldehyde can be employed within certain limits, for the quantitative determination of indene.

When indene in benzene solution is shaken with several per cent. of concentrated sulphuric acid, it is converted into para-indene $(C_9H_8)_x$ (where $x = 4$?) a resin-like body. This is also precipitated, mixed with para-coumarone in connection with the washing of heavy naphtha; and is obtained when indene or fractions containing indene are heated under a reflux condenser; under similar conditions coumarone forms only a trace of resin Together with the solid polymerised indene, there is found in lesser quantity a thick oil which with considerable certainty can be taken as being *di indene.*

Indene can be directly obtained from heavy naphtha or from the resin. In the latter case, however, the yield is very bad, as depolymerisation is accompanied by separation of hydrogen or the wandering of hydrogen atoms. One molecule of para-indene does not give 4 molecules of indene, but truxene and hydrindene according to the formula[1]

$$3(C_9H_8)_4 = 2\ C_{27}H_{18} + 6C_9H_{10}.$$

Truxene—



$$\begin{array}{llll} C_6H_4\text{——} & C = & C - & CH_2 \\ | & | & | & | \\ CH_2\text{——} & C = & C - & C_6H_4 \end{array}$$

(Di-molecular formula as given by Beilstein), m.p 365° C—is colourless in the pure state after distillation. The distillation, however, is accompanied by considerable difficulties, as the substance boils at a very high temperature, and sublimes to a considerable extent. Usually the hydrocarbon is obtained in the condition of fine, light, tangled mass of needles of a golden yellow or orange-red colour. It dissolves with great difficulty in the usual solvents, but to the greatest extent in boiling cumene. It can be obtained fairly easily from pure indene resin by dry distillation and extraction of the residue, and is certainly present in coal tar pitch—perhaps even in considerable quantities—although it has not been isolated from this source.

Truxene was first prepared by Liebermann from truxone $(C_9H_6O)_3$ by heating the latter for two hours with red phosphorous and hydriodic acid at 180° C. Truxone was obtained by the action of fuming sulphuric acid on truxylic acid $(C_8H_7COOH)_n$.[2]

It is not soluble in the ordinary solvents and only to a small extent in boiling xylene, chloroform, aniline, and nitro-benzene.

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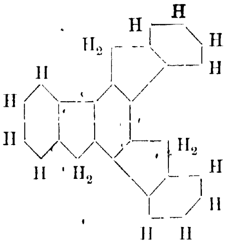
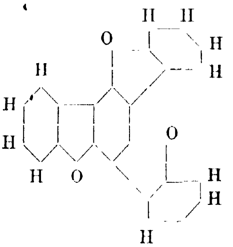
[1] Weger and Billman, *Ber.*, 1903, 640.

[2] *Ber.*, **22**, 784; **23**, 317; Hausmann, *Ber.*, **22**, 2022.

Truxene is also considered to be $(C_9H_6)_3$ tri-ortho-benzylene benzene:



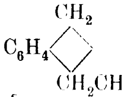
Truxene (trimolecular formula as given by Weger).



Truxene Quinone.

By oxidation with chromic acid there is formed *truxene quinone*, tri-ortho-benzylene benzene $(C_9H_4O)_3$, an orange-yellow substance of similar characteristics as truxene itself. Thus, truxene and its quinone are derived from benzene and not from cyclobutadiene [1]

Hydrindene—



$$C_6H_4\begin{cases}CH_2\\CH_2CH_2\end{cases}$$

b.p. 176–176·5° C.; sp. gr. (15° C.): 0·957—is prepared from indene by reduction with sodium and ethyl alcohol; it can, however, be obtained more cheaply in other ways, as, for instance, from heavy naphtha. According to Moschner,[2] it occurs to the extent of 2·5 per cent in the cumene fraction; but it is obtained much more advantageously from heavy naphtha resin, indene resin, or technical coumarone resin,[3] from which it is prepared at high temperatures by the reaction described already.

It is sulphonated but not polymerised by concentrated sulphuric acid. Its saturated 5-membered ring reacts like an open chain. The sulphonic acid salts and several other derivatives have been examined in some detail by Spilker.[4] It oxidises fairly quickly in the air. By reduction with nickel and hydrogen (Sabatier) hydrindene is converted into a dicyclic naphthene—1 : 9, 1 : 6—dicyclononane—octohydrindene C_9H_{16}.[5]

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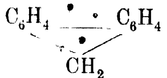
[1] Compare also Michael, *Ber.*, 39, 1910.

[2] *Ber.*, 33, 737.

[3] Kramer and Spilker, *Ber.*, 33, 2257.

[4] *Ber.*, 26, 1538.

[5] Eijkman, *Chem. Weekblad*, 1903, No. 1; see also Thiele, *Ber.*, 33, 771.

Fluorene— 

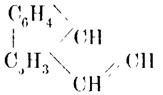
$C_6H_4 \cdot C_6H_4$ / CH_2

m.p. 116° C.; b.p. 295° C. (cor.)—is a colourless substance crystallising in leaflets, from alcohol, possessing a violet fluorescence. It is easily soluble in ether, benzene, and carbon disulphide.

It contains a reactive methylene group whereby it forms compounds with oxalic ester[1] and with potassium[2]; it forms a sodium compound with sodamide at 150° and with sodium at 200°.[3] It reacts with benzaldehyde forming benzal fluorene[4]; with alkyl nitrites and nitrates.[5] Oxidation with chromic acid leads to the formation of fluorenone, a diphenylene ketone.

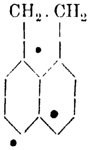
Fluorene is obtained from its particular coal tar fraction by heating with potassium hydroxide at 260–300° and decomposing the lower potassium-fluorene layer with water[6] or from the corresponding sodium compound.[7] Although the property of combining with potassium hydroxide is possessed by very few coal tar hydrocarbons other than fluorene, this substance is not easy to obtain absolutely chemically pure,[8] because potassium fluorene always retains a little phenanthrene which is not removed by the passage of steam without the potassium fluorene itself being decomposed to a considerable extent. Moreover, during fusion with potassium hydroxide, hydrogen is evolved, and there can be traced the formation of ortho-phenyl benzoic acid, which regenerates the 5-membered ring by the action of concentrated sulphuric acid, being converted into fluorene.

Fluorene has not found any extended application in commerce, although if required large quantities could be delivered.

Fluoranthene— 

C_6H_4, CH, C_6H_3, CH, CH

m.p. 109° C.; b.p. 250° C. (at 60 mm.)—crystallises in large, brilliant tablets and in needles. It was discovered in coal tar by Fittig and Gebhard,[9] and its constitution has been established by Fittig and Liebmann.[10] It dissolves readily in the usual solvents.

Acenaphthene— 

m.p. 95° C.; b.p. 278° C. (cor.)—occurs in coal tar in appreciable quantities, where it was first found by Berthelot in 1867.[11] It contains a saturated 5-membered ring, and crystallises from alcohol in strikingly beautiful long needles, which distinguishes it from fluorene and other hydrocarbons of similar boiling point; from heavy tar oils it is obtained in the form of hard brittle crystals. When oxidised it yields acenaphthene quinone, naphthalic acid, and finally, hemimellitic acid. Lately acenaphthene has been employed in the form of its brominated quinone as a red vat dye.[1] When heated with sulphur, acenaphthene is converted into trinaphthylene benzene,[2] a substance which is probably present in pitch. When treated with lead oxide it yields acenaphthylene,[3] which should also exist in tar.

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[1] W. Wislicenus, *Ber.*, **33**, 771.

[2] Weissgerber, *Ber.*, **34**, 1659.

[3] Weissgerber, *Ber.*, **41**, 2914.

[4] Thiele and Henle, *Liebig's Ann.*, **347**, 290.

[5] Wislicenus and Waldmuller, *Ber.*, **41**, 3334.

[6] A.-G. fur Teer- und Erdol-Industrie, D.R.P. 124,15

[7] Ges. fur Teerverwertung, D.R.P. 203,312.

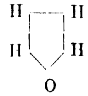
[8] Doring, *Ber.*, **36**, 878.

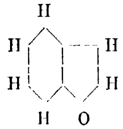
[9] *Liebig's Ann.*, **193**, 142.

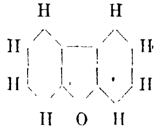
[10] *Liebig's Ann.*, **200**, 3.

[11] *Z. f. Chemie*, 1867, 714.

Among the *neutral substances which contain oxygen included in the ring*, the 6-membered ring series has not yet been observed with certainty in tar, at least in its simplest form. Among the *5-membered ring* compounds are the following members:—


Furane,
C_4H_4O


Coumarone,
C_8H_6O


Diphenylene Oxide,
$C_{12}H_8O$

The first two bodies show great tendency to reaction and polymerisation on account of the double bond in the 5-ring similar to the substances in the cyclopentadiene series, for this reason diphenylene oxide is fairly indifferent in its behaviour.

Furane, C_4H_4O, b.p. 32° C., has so far only been identified in pine-wood tar.

Coumarone—C_8H_6O, liquid at −18° C.; b.p. 172° C. (cor.); specific gravity 1·096—was first prepared by Fittig and Ebert[4] from coumarilic acid, and was later discovered in coal tar by Kramer and Spilker.[5] It is prepared from the heavy naphtha fraction, boiling at 165–175° C., by precipitation with picric acid, and decomposition of the picrate.[6]

Coumarone reacts with bromine, concentrated sulphuric acid, etc., similar to indene. Concentrated sulphuric acid converts it into the (?) tetramolecular "para-coumarone," which is a yellowish-brown brittle resin.

Coumarone resin of commerce, which is usually somewhat softer, is obtained industrially in connection with the washing of heavy naphtha, and contains, as might be expected, para-indene and small quantites of other bodies. It is employed in the preparation of varnishes, and is particularly valued on account of its completely neutral nature; in many other cases also, it replaces the more expensive colophonium which has a somewhat acid character.

During destructive distillation, coumarone resin behaves quite similarly to para-indene—a portion is depolymerised, regenerating coumarone; another portion undergoes wandering of hydrogen atoms, and is converted into substances poorer and richer in hydrogen, comparable to the change of polyindenes into truxene and hydrindene; and finally, a third portion is more profoundly decomposed, accompanied by the breaking down of the 5-membered ring, whereby ethyl benzene and acid oils are formed. These consist mainly of phenol with some ortho-ethyl phenol, as coumarone resin contains oxygen, which indene resin does not. The decomposition products consist of thick oils; and among the higher boiling portions which distil with difficulty in steam, there exist, with great probability, di-coumarone and di-indene. In the residues, there exist truxene-like substances, but containing oxygen, which remain behind as a soft blackish-brown difficultly soluble powder when the coumarone pitch is treated with xylole and the like, and which probably have a composition closely similar to that of the free carbon in ordinary pitch.

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[1] Baseler Chem. Fabrik zu Basel, D.R.P. 196,349 and 198,510.

[2] Rehlander, *Ber.*, **36**, 1583; Dziwonsky and Bachmann, *Ber.*, **36**, 962 and 3768.

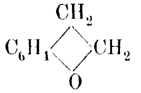
[3] Behr and Dorp, *Liebig's Ann.*, **172**, 273.

[4] *Liebig's Ann.* **216**, 168.

[5] *Ber.*, **23**, 78.

[6] A. G. fur Teer- und Erdol-Industrie, D.R.P. 53,792.

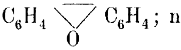
Hydrocoumarone—



$C_6H_4\langle{}^{CH_2}_{O}\rangle CH_2$

still liquid at the temperature of an ice and salt mixture; specific gravity (23° C.): 1·0649, which corresponds to hydrindine—is, without doubt, present in the distillation of resin and also in heavy naphtha; but it has not yet been isolated from these substances. It has, however, been synthesised,[1] from coumarone, sodium, and ethyl alcohol, when ortho-ethyl phenol is formed as a by-product. The reduction with sodium is brought about only under the most careful following of the exact conditions prescribed. Usually the yield in hydrocoumarone is very bad, but it has easily been obtained by the method of Sabatier and Senderens, when ortho-ethyl phenol is again met with as a by-product. It is a colourless oil, soluble in the usual solvents, and almost insoluble in water.

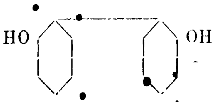
Diphenylene Oxide—



$C_6H_4\underset{O}{\diagdown\!\diagup}C_6H_4$; m.p. 86–87° C.; b.p. 276° C. (uncor.)—is a white substance crystallising in leaflets and showing a blue fluorescence. It is very stable against oxidising and reducing reagents. It has been synthesised by many different methods, and has been found in tar by Kramer and Weissgerber.[2] As diphenylene oxide does not possess acidic properties and therefore does not lend itself to being extracted, it is separated pure from fluorene and other hydrocarbons which boil at a similar temperature only with great difficulty. It is most easily obtained in considerable quantity from ortho-diphenol (ortho ortho-dihydroxydiphenyl).

Ortho-diphenol is formed from diphenylene oxide (but not from fluorene as previously thought) during the production of fluorene by the potassium alkali fusion[3] and from the fusion of anthracene with potassium hydroxide.[4] Further, it remains after decomposition of potassium-fluorene and potassium-carbazole and can be precipitated by acids from the alkaline liquid.[5]

Ortho-diphenol (Ortho-ortho-dihydroxydiphenyl)—



m.p. 109° C.; b.p. 315° C. (uncor.)—crystallises in compact crystals and is difficult to obtain completely colourless. It is easily soluble in alcohol and ether, but dissolves with difficulty in cold benzene and in water. From the latter it is obtained in leaflets containing water, m.p. 73–75° C. Being a polyvalent phenol, it is taken up by soda solution in the cold, and gives a reddish-violet colour with ferric chloride.

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[1] Alexander, *Ber.*, 25, 2409. [2] *Ber.*, 34, 1662.

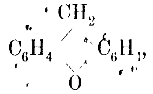
[3] A.-G. fur Teer- und Erdol-Industrie, D.R.P. 124,150.

[4] A.-G. fur Teer- und Erdol-Industrie, D.R.P. 111,359.

[5] A.-G. für Teer- und Erdol-Industrie, D.R.P. 130,679.

To this group of oxides belongs:

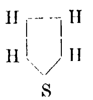
Xanthene, the anhydride of ortho-dihydroxydiphenyl methane, diphenyl-methane oxide



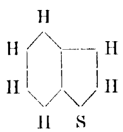
$$C_6H_4 \overset{CH_2}{\underset{O}{\diagup\diagdown}} C_6H_4,$$

which is the only representative in tar of a 6-membered ring containing oxygen. It has not yet been directly isolated from tar, but its presence is rendered probable by the fairly definite substantiation of the existence of orthodihydroxydiphenyl methane, a companion of the above mentioned orthodihydroxydiphenyl.

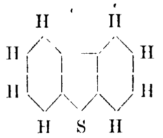
The following *sulphur compounds* correspond with the above described oxides:—



Thiophene, C_4H_4S



Thiocoumarone, C_8H_6S



Diphenylene Sulphide, $C_{12}H_8S$

Only thiophene and its homologues have any importance.

Thiophene—C_4H_4S; b.p. 84·1° C.; specific gravity (15° C.): 1·070—is very similar to benzene. It was discovered by V. Meyer in coal tar benzole[1] and can be removed by concentrated sulphuric acid,[2] or by basic mercuric sulphate.[3] It is best obtained[4] by diluting the sulphuric acid immediately after its employment in washing benzole, and steam distilling the diluted acid. When two to three times the quantity of water is employed for the dilution, purer thiophene is obtained than when only an equal quantity of water is used, as in the first case, the accompanying sulphonic acids of trimethyl benzene, and particularly of xylene (toluene sulphonic acid appears not to be formed, or is decomposed only with great difficulty), are not split by such strong dilution. The amount of thiophene present in benzole and its quantitive determination have already been dealt with.

The homologues of thiophene—the thiotolenes and thioxenes—accompany toluene and xylene respectively, and have been obtained from the acid employed in washing toluole and xylole in a similar manner as has thiophene.[5] (For quantitive test for thiotolene, see "Toluene").

Thiocoumarone—(Thionaphthene); C_8H_6S; m.p. 31° C.—has so far only been prepared synthetically, but probably occurs in naphthalene oil, together with naphthalene of which the boiling point is identical.

Diphenylene Sulphide, $C_{12}H_8S$, has also not yet been isolated from tar, but probably accompanies the corresponding oxide, as sulphur is always present in the potassium alkali melt of fluorene.

A final group of neutral constituents of coal tar is formed by certain substances containing nitrogen, in which the ring containing the *nitrogen* or the imide group in a *5-membered ring*. The 6-membered ring containing nitrogen is characterised by strongly basic properties (Aniline, etc.).

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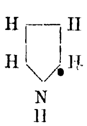
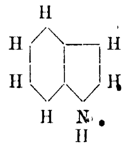
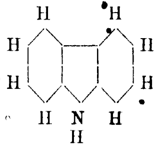
[1] *Ber.*, 16, 1465.
[2] V. Meyer, *Ber.*, 17, 2641.
[3] Compare Volhard, *Liebig's Ann.*, 267, 72.
[4] Schulze, *Ber.*, 18, 497.
[5] Schulze, *Ber.*, 17, 2852.



Pyrole,
C_4H_5N



Indole,
C_8H_7N



Carbozole,
$C_{12}H_9N$

Pyrrole—C_4H_5N ; b.p 133° C. ; specific gravity, 1 077—was discovered in coal tar by Runge.[1]

It is readily soluble in ether and alcohol, and turns brown in the air. It is a stable substance, but is polymerised into *tripyrrole* by the passage of dry hydrogen chloride into it in ethereal solution. When heated to 300° C., tripyrrole decomposed into ammonia, pyrrole and indole.

Indole, C_8H_7N, a weak base, has not yet been identified in coal tar.

Carbazole—$C_{12}H_9N$, m p. 238° C. ; b.p. 355° C.—is present in tar in considerable quantities, and has a certain technical importance. It crystallises in white leaflets, and is intimately associated with anthracene, from which it is removed with great difficulty by solvents, except pyridine bases (see above under Anthracene). On the other hand, the separation is easily effected by potassium alkali melt. The potassium compound of carbazole has long been known.[2]

Carbazole resembles a hydrocarbon in giving a sulphonic acid and a nitro-compound (compare, for instance, E. Wirth, D.R.P. 128,853). It can be identified by a number of colour reactions.

Dinitrocarbazole is easily converted into para-diamidocarbazole, $C_{12}H_7(NH_2)_2$, from which, by coupling with salicylic acid, is obtained the substantive dye stuff, carbazole yellow.

Diiodocarbazole, $C_{12}H_7I_2N$, is employed as an antipyretic.[3] Hydro- and Nitroso- compounds are known.

Phenyl para Naphthyl Carbazole—$C_{16}H_{11}N$; m.p. 330° C.—is obtained by subliming the residue from distilling crude anthracene, and is white when pure. It does not dissolve to any important extent in, but imparts an intense blue fluorescence to the usual solvents.

Like the pure hydrocarbons, the oxygen, nitrogen and sulphur compounds are present in coal tar to an extent determined not only by the conjunction of three rings, but by the benzene ring being substituted by a naphthalene ring, as, for example, in the case of naphthyl-phenyl-benzene. These very high boiling bodies are to be found in pitch.

Acid Substances—Phenols are characterised by containing *oxygen in the side chain*, and many homologues, including the two naphthols, have been identified in tar ; but not, however, the anthrols. Polyvalent phenols with one side chain, such as brenzcatechin, have not yet been found in coal tar, but only in such material such as low temperature distillation tar.[1] These acid oils, the phenols, which may constitute as much as 40 per cent. of their particular fractions, are absent only in the lowest, because the first representative, carbolic acid, boils at 184°; but they are found in the highest boiling fractions.

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[1] *Poggedorf's Ann.*, 31, 67.

[2] Græbe, 1880, *Liebig's Ann.*, 202, 22.

[3] Classen, D.R.P. 81,929.

Phenol—$C_6H_5.OH$; b.p. 183–184° (cor.); s.p. 40·5°—is of very great technical importance, and is one of the most valuable constituents of coal tar. It is obtained crude by the extraction of a fraction more or less restricted in range of distillation—carbolic oil—by means of sodium hydroxide solution, and the neutralisation of this by means of carbonic or sulphuric acid. The separation of phenol from the cresol is based on the stronger acidity of the former,[2] followed by fractional distillation and by partial solidification.

It is, however, very difficult to obtain it chemically pure, in which condition it remains colourless and solid. The smallest quantity of impurities causes it to turn red, and to become moist when standing in contact with the air, especially in summer-time. The solidification point of phenol, which is the most important measure of its value in industry, is depressed to an extraordinary extent by the presence of quite small quantities of water or cresol. Pure phenol must, of course, dissolve to a completely clear solution, and must not show any turbidity when diluted to any extent. The Pharmacopœia requires that acidum carbolicum shall melt from 39–40° and dissolve to a clear dilution in 15 parts of water. Further, a liquid carbolic acid, "acidum carbolicum liquifactum," is officinal.

The most sensitive test reagents for phenol are bromine water, or a solution of mercuric nitrate containing nitrous acid (Millon's reagent).

The quantitative determination of phenol in the presence of cresols can be made with considerable accuracy by the methods of Weiss[3] and of Fox.[4]

The employment of phenol for purposes of disinfection is well known; it is also used in the preparation of dyes, mono- and di-nitrophenol, and picric acid. The latter can also be manufactured from benzene by the conversion of dinitrochlorobenzene into dinitrophenol. An important quantity of phenol is used also in the preparation of salicylic acid. In commerce is found not only coal tar carbolic acid, but also a synthetic product prepared from sodium benzene sulphonate.[5]

Phenol Hydrate—$C_6H_5OH.H_2O$; m.p. 17·2° C.—contains 16·07 per cent. water, which begins to separate at 100° C.

Cresol, $C_6H_4(CH_3)(OH)$, exists in the form of three isomers in the average proportions of ortho-, 40 per cent., meta-, 35 per cent, and para-, 25 per cent.: each of these is produced on a commercial scale.

Ortho-Cresol, (1 : 2); m.p. 30° C.; b.p. 191° C. (cor.); specific gravity (15·5° C.): 1·0518.

Meta-Cresol, (1 : 3), solidifies only with difficulty, after which it melts at 4° C.; b.p. 203° C. (cor.); specific gravity (15·5° C.): 1·0387.

Para-Cresol, (1 : 4); m.p. 36° C.; b.p. 202° C. (cor.); specific gravity (15·5° C.): 1·0388.

The separation of the three cresols from tar has been the subject of a very large amount of work, dealing mostly with the separation of meta- and para-cresols since the ortho-compound can be sufficiently well obtained by fractional distillation.

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[1] Bornstein, *Ber.*, 35, 4324.

[2] Compare Muller, *Z. f. Chem.*, 1865, 270; and in greater detail, Lunge-Köhler *Industries des Steinkohlenteers*, 4th edition, p. 515.

[3] *J. Ind. and Eng. Chem.*, 1917, 569.

[4] *J. Soc. Chem. Ind.*, 1917, 842.

[5] Ney, reported in *Chem. Trade Journal*, 1915, 361.

The most important processes are covered by the following patents: Riehm, D.R.P. 53,307, makes use of the different solubilities of the barium salts; Lederer, D.R.P. 79,514, employs chloracetic acid; Byck, D.R.P. 100,418, treats the material with various salts; Raschig, D.R.P. 112,545, sulphonates the mixture of meta- and para-cresols, and separates by crystallisation of the para-sulphonic acid, or of its sodium salt; Raschig, D.R.P. 114,975, treats the mixture of sulphonic acid with superheated steam at 120–185°, whereby the meta-cresol sulphonic acid being decomposed, meta-cresol distils over, whilst the para-sulphonic acid remains unchanged; Rutgers, D.R.P. 137,584, and 141,421, separates para- from meta-cresol by means of anhydrous oxalic acid, the former being precipitated in the form of the solid oxalic ester; Ladenburg, D.R.P. 148,703, carries out the separation by means of sodium bisulphate containing pyrosulphate; Ladenburg, D.R.P. 152,652, prepares meta-cresol from crude cresol by means of the small solubility of the neutral calcium meta-cresolate; finally, Gentsch, D.R.P. 156,761, and 157,616 separates the cresols by means of potash.

Schulze, who separates the three isomers of coal tar cresol by fractional saturation or preparation of the potassium sulphonates[1], estimates the content as being ortho-cresol 35 per cent., meta-cresol 40 per cent., para-cresol 25 per cent. These figures are undoubtedly accurate in specific cases, but it is incorrect to assume that they hold good for commercial cresols in general, as these vary according to the origin of the tar, the method of working up, and the distillation range of temperature.

The "100 per cent. liquid carbolic acid" which constitutes commercial cresol, and consists of a mixture of the three isomeric cresols, more or less phenol, and some ethyl phenol and xylenol, is employed almost entirely for purposes of disinfection.

Attempts have been made to overcome the disadvantage of its low solubility in water by means of numerous additions, such as linseed oil soap (liquor cresoli saponatus), resin soap, sulphuric acid, salicylic acid salts, sulphonic acid salts, and many others.

On the relative toxic power and power of disinfection, an enormous amount of work has been done and described without, till now, an agreement having been attained.

Attempts have been made to reduce cresol by means of hydrogen and nickel[2] to cyclohexanol or cyclohexanone for employment as a substitute for camphor,[3] or for use as a solvent, in which case the cost of reduction would be much too high. A cresol fraction, rich in meta-cresol, is employed in considerable quantities in the explosive industry for the preparation of trinitro-meta-cresol—"cresylite." A very good method for the determination of meta-cresol is that of Raschig,[4] which consists of treating a solution of cresol in sulphuric acid with concentrated nitric acid, whereby the meta-compound is trinitrated, and the ortho- and para-cresols are oxidised to oxalic acid. The mode of carrying out this reaction is the so-called French method, which is the same in principle, but is decidedly to be preferred.

Lately, cresol as well as phenol has been condensed with formaldehyde for the preparation of artificial resins, ebonite substitutes, and the like. As these materials, made out of ordinary cresol, have too strong an odour, the more feebly smelling pure ortho-cresol is employed, with which very useful results have actually been obtained.[1]

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[1] *Ber.*, 20, 410.

[2] Sabatier and Senderens.

[3] Raschig, D.R.P. 174,914.

[4] *Z. f. angew. Chem.*, 1900, 759.

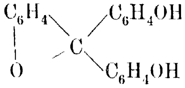
The Dimethyl Phenols—$C_6H_3(CH_3)_2(OH)$, 1 : 3 : 5,—and 1 : 2 : 4 *xylenols* have been identified in tar.

*α- and β-***Naphthol,** $C_{10}H_7OH$, are found in tar (compare the notable work of Schulze),[2] but both are far more cheaply prepared synthetically from naphthalene.

α-Naphthol—m.p. 94–96° C.; b.p. 278–280° C.; specific gravity 1·224—consists of brilliant needles. It volatilises in steam and is sparingly soluble in hot water, but easily soluble in the usual solvents.

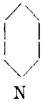
β-Naphthol—m.p. 122–123° C.; b.p. 291° C.; specific gravity 1·217—volatilises sparingly in steam, but is as soluble in various liquids as α-naphthol.

Rosolic Acid—$C_{19}H_{14}O_3$

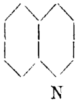


was first discovered in coal tar by Runge in 1834,[3] though it had probably been formed by subsequent chemical treatment. Its main interest lies in its being the most likely substance responsible for the pink colour which is slowly formed in phenol.

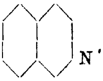
The *basic constituents of coal tar* are present in all fractions; they are extracted by dilute sulphuric acid, and precipitated from their sulphuric solution by means of ammonia or sodium hydroxide. The following groups of substances contain the nitrogen atom included in the ring:—



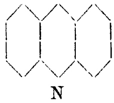
Pyridine,
C_6H_5N



Quinoline,
C_9H_7N



Isoquinoline,
C_9H_7N



Acridine,
$C_{13}H_9N$

Pyridine—C_6H_5N, s.p. −42° C.; b.p. 115° C.; specific gravity (15° C.): 0·978—was discovered in coal tar by Greville Williams. It constitutes the most important body in the bases employed on the Continent for denaturing purposes where, according to the requirements of the Inland Revenue, it shall distil 90 per cent. from 90–160°. An industrial quality of pyridine, b.p. about 115–118° C., can be employed for the preparation of the pure substances by means of the zinc double salt.

It behaves like a true alkali, precipitating hydroxides from salts of the metals, and forming stable salts soluble in water. It resists the action of fuming nitric and chromic acids.

Pyridine is employed as a solvent, for the purposes of combining with acids in certain reactions, and for the preparation of piperidine, a change which can easily be carried out electrolytically.[4] This reduction of pyridine to piperidine has not yet been achieved by Sabatier's method.

The three **Methyl Pyridines,** α-, β-, and γ-.[5]

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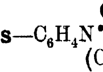
[1] Bayer and Co., D.R.P. 201,261.

[2] *Liebig's Ann.* **227**, 143.

[3] *Pogg. Ann.* **31**, 65, 512; **32**, 308, 323.

[4] Merck, D.R.P. 90,308, 104,664.

[5] See also Eckert and Loria, *Monatsh.*, 1917, **38**, 225; *J. Chem. Soc.*, 1918, Abstr. i., 79.

Picolines— $C_6H_4N\overset{C}{\underset{(CH_3)}{|}}$; b.p. 135° C.; specific gravity (0°C.): 0·9613—have all been identified in tar; of these the α-compound can be obtained approximately pure by fractional distillation.

α-Picoline, b.p. 133·5 (cor.); specific gravity (10° C.): 0·952.

β-Picoline, b.p. 143·5 (cor.); specific gravity 0·9726.

γ-Picoline, b.p. 142·5–144·5 (cor.); specific gravity 0·9742.

Dimethyl Pyridines (Lutidines), $C_6H_3N.(CH_3)_2$, the **Trimethyl Pyridines (Collidines)**, $C_6H_2N(CH_3)_3$, and the **Tetramethyl Pyridines (Parvolines)**, $C_6HN(CH_3)_4$, are also present in coal tar, but are difficult to obtain pure. All these bodies are accompanied by primary bases, such as aniline, which can be removed by diazotizing.

Quinoline—C_9H_7N; b.p. 239–240° C.; specific gravity 1·081—occurs in appreciable quantities in coal tar, but this source is competed with by its synthetic production from nitrobenzene, aniline, glycerine, and sulphuric acid. It is used for the preparation of the ortho- and para-sulphonic acid, and of hydroxquinoline. Quinoline is accompanied by

Isoquinoline—C_9H_7N; m.p. 20° C.; b.p. 236–237° C.—to the extent of about 1 per cent., which boils at almost exactly the same temperature. It is solid, having a clinging odour, quite different from quinoline. It was first discovered in coal tar by Hoogerwerf and Van Dorp,[1] by separation from quinoline by means of recrystallisation of the acid sulphate, whereby a very valuable preparation was obtained. Isoquinoline is employed in the production of a very valuable red dye—quinoline red—which is employed in photography, and for staining microscopical preparations.

α-**Methyl Quinoline** (Quinaldine), $C_9H_6N(CH_3)$, b.p. 238–239° C., and β-**Methyl Quinoline** (Lepidine), $C_9H_6N(CH_3)$, b.p. 250–257° C., specific gravity (15° C.), 1·072, are present in coal tar.

Acridine—$C_{13}H_9N$; m.p. 107° C. or 111° C.; b.p. over 360° C.—crystallises in fine, clear, yellow prisms, and is to be found in crude anthracene. It is a stable substance and is readily soluble in ether, alcohol, carbon disulphide and hydrocarbons. It is intensely irritating to the mucous membrane and to the skin, so that its preparation is a somewhat unpleasant operation. At the present time, it is a relatively costly product, but could be prepared at a cheaper price if demand were greater.

Other bases occur in coal tar in which the nitrogen is present in the side chain, such as—

Aniline—$C_6H_5NH_2$; s.p. − 8° C.; b.p. 182° C.; sp. gr. (16° C.): 1·020—occurs to only a small extent in coal tar, so that this source is negligible as compared with the synthetic production.

In addition to the compounds described up to the present, there are to be found in coal tar, ketones, nitriles, paraffins, olefines, and numerous hydrogenated substances. With the exception of benzonitrile, none of these substances are of value.

Acetone was obtained by Heusler[2]; **Methyl ethyl ketone** by Schulze[3]; and **Acetophenone** by Weissgerber.[4]

Benzonitrile, C_6H_5CN, was found in carbolic oil by Kramer and Spilker.[5] According to the D.R.P. 109,122 of the A.-G. fur Teer- und Erdöl-

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[1] *Recueil*, 4, 125; 5, 305.

[2] *Ber.*, 28, 488.

[3] *Ber.*, 20, 41[illegible].

[4] *Ber.*, 36, 754.

[5] *Ber.*, 23, 78.

Industrie, it is converted into benzoic acid by hydrolysis with sodium hydroxide solution of specific gravity 1·4, the resulting preparation being distinguished by its freedom from chlorine.

Of the **Aliphatic Hydrocarbons** a number of the members of the saturated series have been isolated and identified as well as of the unsaturated.

There are also present **Hydrogenated Bodies** other than the above mentioned, such as hydrobenzene, hydronaphthalene and hydroacridine. It has been found that the specific gravities of paraffin, isolated from the various fractions, is higher than would be expected from a comparison with mineral oil with paraffin fractions of the same boiling points. There is considerable reason for thinking this to be due to the presence of **Naphthenes,** a series of polymethylene hydrocarbons consisting of simple and substituted rings.[1] These substances are unaffected by 100 per cent. sulphuric acid, but are attacked by oleum with the generation of sulphur dioxide.

ABBREVIATIONS.

b.p.	Boiling point.	f.p.	Freezing point.
s.p.	Solidifying point.	sp. gr.	Specific gravity.

Note.—There is much interesting and careful work on Coal Tar details published in the two American journals: *Metallurgical and Chemical Engineering* and *Journal of Industrial and Engineering Chemistry.*

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[1] Compare, for instance, Ahrens, *Z. f. angew. Chem.*, 1908, 1411.

APPENDIX II.

INTERNATIONAL ATOMIC WEIGHTS. (1918).

With Multiples.

			×2	×3
Aluminium	Al	27·1	54·2	81·3
Antimony	Sb	120·2	240·4	360·6
Argon	A	39·88	79·76	119·64
Arsenic	As	74·96	149·92	224·88
Barium	Ba	137·37	274·74	412·11
Bismuth	Bi	208·0	416	624
Boron	B	11·0	22	33
Bromine	Br	79·92	159·84	239·76
Cadmium	Cd	112·40	224·8	337·2
Cæsium	Cs	132·81	265·62	398·43
Calcium	Ca	40·07	80·14	120·21
Carbon	C	12·005	24·010	36·015
Cerium	Ce	140·25	280·5	420·75
Chlorine	Cl	35·46	70·92	106·38
Chromium	Cr	52·0	104	156
Cobalt	Co	58·97	117·94	176·91
Columbium	Cb	93·1	186·2	279·3
Copper	Cu	63·57	127·14	190·71
Dysprosium	Dy	162·5	325·0	487·5
Erbium	Er	167·7	335·4	503·1
Europium	Eu	152·0	304	456
Fluorine	F	19·0	38	57
Gadolinium	Gd	157·3	314·6	471·9
Gallium	Ga	69·9	139·8	209·7
Germanium	Ge	72·5	145	217·5
Glucinum	Gl	9·1	18·2	27·3
Gold	Au	197·2	394·4	591·6
Helium	He	4	8	12
Holmium	Ho	163·5	327·0	490·5
Hydrogen	H	1·008	2·016	3·024
Indium	In	114·8	229·6	344·4
Iodine	I	126·92	253·84	380·76
Iridium	Ir	193·1	386·2	579·3
Iron	Fe	55·84	111·68	167·52
Krypton	Kr	82·92	164·84	247·76
Lanthanum	La	139·0	278	417
Lead	Pb	207·20	414·4	621·6
Lithium	Li	6·94	13·88	20·82
Lutecium	Lu	175·0	350	525
Magnesium	Mg	24·32	48·64	72·96
Manganese	Mn	54·93	109·86	164·79
Mercury	Hg	200·6	401·2	601·8
Molybdenum	Mo	96·0	192	288

INTERNATIONAL ATOMIC WEIGHTS—*continued*.

			×2	×3
Neodymium	Nd	144·3	288·6	432·9
Neon	Ne	20·2	40·4	60·6
Nickel	Ni	58·68	117·36	176·04
Niton	Nt	222·4	444·8	667·2
Nitrogen	N	14·01	28·02	42·03
Osmium	Os	190·9	381·8	572·7
Oxygen	O	16·00	32	48
Palladium	Pd	106·7	213·4	320·1
Phosphorus	P	31·04	62·08	93·12
Platinum	Pt	195·2	390·4	585·6
Potassium	K	39·10	78·2	117·3
Praseodymium	Pr	140·9	281·8	422·7
Radium	Rd	226·0	452	678
Rhodium	Rh	102·9	205·8	308·7
Rubidium	Rb	85·45	170·9	256·35
Ruthenium	Ru	101·7	203·4	305·1
Samarium	Sa	150·4	300·8	451·2
Scandium	Sc	44·1	88·2	132·3
Selenium	Se	79·2	158·4	237·6
Silicon	Si	28·3	56·6	84·9
Silver	Ag	107·88	215·76	323·64
Sodium	Na	23·00	46	69
Strontium	Sr	87·63	175·26	262·89
Sulphur	S	32·06	64·12	96·18
Tantalum	Ta	181·5	363	544·5
Tellurium	Te	127·5	255	382·5
Terbium	Tb	159·2	318·4	477·6
Thallium	Tl	204·0	408	612
Thorium	Th	232·4	464·8	697·2
Thulium	Tm	168·5	337	505·5
Tin	Sn	118·7	237·4	356·1
Titanium	Ti	48·1	96·2	144·3
Tungsten	W	184·0	368	552
Uranium	U	238·2	476·4	714·6
Vanadium	V	51·0	102	153
Xenon	Xe	130·2	260·4	390·6
Ytterbium (Neoytterbium)	Yb	173·5	347	520·5
Yttrium	Yt	89·0	178	267
Zinc	Zn	65·37	130·74	196·11
Zirconium	Zr	90·6	181·2	271·8

There has been no change from 1917.

STANDARD SOLUTIONS FOR VOLUMETRIC ANALYSIS.

Normal (N/1) *Hydrochloric Acid*, containing 36·46 grammes of HCl per litre, and prepared by diluting 82·3 c.c. of concentrated acid with water to make 1 litre, the solution being standardised by means of decinormal alkali.

Normal (N/1) *Sulphuric Acid*, containing 49·04 grammes of H_2SO_4 per litre, and prepared by diluting 52 to 53 grammes of concentrated acid with water to make 1 litre, the solution being standarised with anhydrous sodium carbonate in presence of methyl orange.

Decinormal (N/10) *Oxalic Acid*, containing 6·302 grammes of $H_2C_2O_4 + 2H_2O$ per litre.

Normal (N/1) *Caustic Potash*, containing 56·16 grammes of KOH per litre, prepared by dissolving about 8 grammes of purest KOH in 200 c.c. of water, eliminating carbonic acid with baryta water and making up the filtrate to 1 litre, the solution being standardised with decinormal acid.

Normal (N/1) *Caustic Soda*, containing 40·06 grammes NaOH per litre, prepared and standardised in the same way as normal caustic potash.

Normal (N/1) *Ammonia*, containing 1·703 grammes of NH_3 per litre, prepared by diluting 9·25 c.c. of 20 per cent. ammonia to 1 litre, the solution being standardised with decinormal acid in presence of luteol.

Decinormal (N/10) *Baryta Water*, containing 8·572 grammes of $Ba(HO)_2$ per litre, and prepared by dissolving about 18 grammes of crystallised barium hydroxide and 1 gramme of barium chloride, filtering the solution out of contact with air, making it up to 1 litre, and standardising with decinormal hydrochloric acid

Normal (N/1) *Sodium Carbonate Solution*, containing 53·05 grammes of anhydrous Na_2CO_3 per litre, and prepared by dissolving 143·12 grammes of crystalline carbonate to 1 litre, the solution being standardised with normal acid.

Normal (N/1) Nitric Acid contains		63·018	grms.	HNO_3	per litre.
Decinormal (N/10) Potassium Permanganate	contains	3·161	,,	$KMnO_4$	per litre.
Decinormal (N/10) ,, Dichromate	,,	4·903	,,	$K_2Cr_2O_7$	,,
Decinormal (N/10) Iodine	,,	12·692	,,	I_2	,,
Decinormal (N/10) Sodium Thiosulphate	,,	24·822	,,	$Na_2S_2O_3.5H_2O$	,,
Decinormal (N/10) Arsenious Oxide	,,	4·948	,,	As_2O_3	,,
Decinormal (N/10) Silver Nitrate	,,	16·989	,,	$AgNO_3$	,,
Decinormal (N/10) Sodium Chloride	,,	5·846	,,	NaCl	,,
Decinormal (N/10) Ammonium Thiocyanate	,,	7·612	,,		
Decinormal (N/10) Potassium Thiocyanate	,,	11 717	,,	KCNS	,,

INDICATORS.

Methyl Orange—1 gramme per litre. Colour pink in presence of acid, and yellow in alkaline solution suitable for titrating hydrochloric, sulphuric, and nitric acids, strong bases, ammonia, soda and borax, but not for fatty acids, oxalic acid, carbonic acid, and boric acid. Small quantity sufficient; not suitable for hot solutions.

Congo Red—Solution consists of 0·5 gramme dye, 90 c.c. water, and 10 c.c. of 96 per cent. alcohol. Colour bluish violet to blue in acid liquids, bright red in alkaline. Suitable for titrating mineral acids, fixed alkalis and alkaline earths, ammonia, alkaloids, but not for weak acids or in hot solutions.

Cochineal—Solution, 3 grammes of whole cochineal extracted with 250 c.c. of 25 per cent. alcohol. Reddish yellow in acid liquid. Violet in alkaline. Suitable for ammonia and mineral acids, but not for organic acids.

Litmus—Solution, 1 : 10, red in acid liquids and blue with violet tinge in alkaline. Suitable for hydrochloric, sulphuric, and nitric acids. Caustic soda and potash, barium hydroxide and ammonia, but not for carbonates, borates, phosphoric acid, or sulphuretted hydrogen.

Rosolic Acid—Solution, 0·5 gramme in 50 c.c. of alcohol, and 50 c.c. of water.

Phenolphthalein—Solution, 1 gramme in 100 c.c. of 96 per cent. alcohol. Colourless in acid liquids, red in alkaline. Suitable for strong bases, acid phosphates, oxalic acid, and other organic and inorganic acids, especially weak ones, but not for weak bases, ammonia or boric acid.

Luteol—Solution, 0·1 gramme in 50 c.c. of 96 per cent. alcohol. Colourless in acid liquids, yellow in alkaline. Suitable for titrating ammonia (4 drops in 50 c.c. of test solution).

Decinormal solutions are prepared with water measured at 15° C., and in order to obtain precise results, the volume of solution consumed in titration should be corrected to that temperature. The factors with which the number of c.c. of decinormal solution consumed should be multiplied in order to obtain that correction are given in the subjoined table.

FACTORS FOR CORRECTING THE VOLUME OF DECINORMAL SOLUTIONS TO 15° C.

Temperature.	Factor.	Temperature.	Factor.
15°C.	1·000000	21°C.	0·999057
16°C.	0·999870	22°C.	0·998857
17°C.	0·999728	23°C.	0·999864
18°C.	0·999576	24°C.	0·984338
19°C.	0·999412	25°C.	0·998207
20°C.	0·999238		

TABLES FOR USE IN VOLUMETRIC ANALYSIS.

Equivalence of Standard Acid Solution.

1 c.c. of Normal Acid corresponds to		Gram.
Ammonia	NH_3	0·01703
Ammonium	NH_4	0·01804
Barium hydroxide	$Ba(OH)_2$	0·08572
Baryta crystals	$Ba(OH)_2+8H_2O$	0·15778
Glycerine (acetin method)	$C_3H_8O_3$	0·03068
Calcium carbonate	$CaCO_3$	0·05006
Calcium hydroxide	$Ca(OH)_2$	0·03707
Calcium oxide	CaO	0·02806
Calcium sulphate	$CaSO_4$	0·06809
Potassium	K	0·03915
Potassium bicarbonate	$KHCO_3$	0·10016
Potassium carbonate	K_2CO_3	0·06915
Potassium hydroxide	KOH	0·05616
Potash	K_2O	0·04715
Magnesium	Mg	0 01218
Magnesium carbonate	$MgCO_3$	0·04218
Magnesia	MgO	0·02018
Sodium	Na	0·02305
Sodium bicarbonate	$NaHCO_3$	0·08406
Sodium carbonate	Na_2CO_3	0·05305
Sodium carbonate, crystals	$Na_2CO_3+10H_2O$	0·14313
Sodium hydroxide	$NaOH$	0·04006
Soda	Na_2O	0·03105
Sodium tetraborate	$Na_2B_4O_7+10H_2O$	0·19115
Nitrogen (in NH_3)	N	0·01401
Malic acid	$C_4H_6O_5$	0·06702
Formic acid	$HCOOH$	0·04602
Succinic acid	$C_4H_6O_4$	0·05902
Hydrobromic acid	HBr	0·08097
Hydrochloric acid	HCl	0·03646
Citric acid	$C_6H_8O_7+H_2O$	0·07003
Acetic acid	$C_2H_4O_2$	0·06003
		0 346
Rosin acids (Twitchell method)	H[illegible]	0·12797
Hydriodic acid	$C_3H_6O_3$	0·09005
Lactic acid	$C_{18}H_{34}O_2$	0·28226
Oleic acid	$C_2H_2O_4+2H_2O$	0 06302
Oxalic acid, crystals	$C_2H_2O_4$	0·04501
Oxalic acid, anhydrous	$KHC_2O_4+C_2H_2O_4$	0·08474
Potassium oxalate	$+2H_2O$	
Palmitic acid	$C_{16}H_{32}O_2$	0·25624
Phosphoric acid (methyl orange)	H_3PO_4	0·0980
Phosphoric acid (phenolphthalein)	H_3PO_4	0·0490
Salicylic acid, crystals	$C_7H_6O_3$	0 13805
Nitric acid	HNO_3	0·06302
Nitric anhydride	N_2O_5	0·05401
Sulphuric acid	H_2SO_4	0·04904
Sulphuric anhydride	SO_3	0·04003
Stearic acid	$C_{18}H_{36}O_2$	0·28427
Tartaric acid	$H_2C_4H_4O_6$	0·07502
Cream of tartar	$KHC_4H_4O_6$	0·18819

Equivalence of Decinormal Permanganate Solution.

1 c.c. of Decinormal $KMnO_4$ Solution (5·662 grams per litre) corresponds to

		Gram.
Lead	Pb	0·01034
Calcium	Ca	0·00201
Iron	Fe	0·00559
Ferrous oxide	FeO	0·00719
Ferric oxide	Fe_2O_3	0·00799
Ferro-ammonium sulphate	$FeSO_4+(NH_4)_2SO_4 + 6H_2O$	0·039217
Ferrous sulphate		
Glycerine (Allen method)	$(FeSO_4+7H_2O)$	0·027805
″		0·0046
		0·00741
Indigotin	$KHC_2O_4+C_2H_2O_4+2H_2O$	0·00635
Potassium tetraoxalate		
Manganese	Mn	0·00275
Manganous oxide	MnO	0·00355
Manganese peroxide	MnO_2	0·00435
Sodium peroxide	Na_2O_2	0·00390
Oxalic acid, crystals	$H_2C_2O_4+2H_2O$	0·00630
Oxalic acid, anhydrous	$H_2C_2O_4$	0·00450
Nitric acid	HNO_3	0·00315
Nitrous acid	HNO_2	0·00235
Oxygen (in acid solution)	O	0·00080
Hydrogen peroxide	H_2O_2	0·00170
Stannous chloride	$SnCl_2+2H_2O$	0·01129

Equivalence of Decinormal Sodium Thiosulphate Solution.

1 c.c. of Decinormal Solution (24·83 grams per litre) corresponds to

		Gram.
Bromine (free)	Br	0·007996
Chlorine (free)	Cl	0·003545
Iron	Fe	0·005588
Ferrous oxide	FeO	0·007188
Ferric oxide	Fe_2O_3	0·007988
Iodine	I	0·012697
Potassium dichromate	$K_2Cr_2O_7$	0·004909
Potassium permanganate	$KMnO_4$	0·003164
Manganese peroxide	MnO_2	0·00435
Oxygen (free)	O	0·00080
Hypochlorous acid	HOCl	0·00262
Chloride of lime	$CaOCl_2$	0·00635
Hydrogen peroxide	H_2O_2	0·00170

Equivalence of Decinormal Arsenious Acid.

1 c.c. of Solution (4·95 grams of As_2O_3 per litre) corresponds to

		Gram.
Bleaching powder, regarded as free chlorine	Cl	0·003545
Bromine	Br	0·007996
Chlorine	Cl	0·003545
Iodine	I	0·012697
Manganese peroxide	MnO_2	0·004350
Sulphuretted hydrogen	H_2S	0·002556

Equivalence of Decinormal Silver Nitrate.

1 c.c. of Solution (16·994 grams per litre) corresponds to

		Gram.
Ammonium bromide	NH_4Br	0·009800
Ammonium chloride	NH_4Cl	0·005349
Ammonium thiocyanide	NH_4CNS	0·007611
Bromine	Br	0·007996
Hydrobromic acid	HBr	0·008097
Chlorine	Cl	0·003545
Cyanogen (Liebig)	CN	0·005202
Hydrocyanic acid	HCN	0·005404
Iodine	I	0·012697
Hydriodic acid	HI	0·012798
Potassium bromide	KBr	0·011911
Potassium chloride	KCl	0·00746
Potassium cyanide (Liebig)	KCN	0·013032
Potassium iodide	KI	0·016612
Sodium bromide	$NaBr$	0·010301
Sodium chloride	$NaCl$	0·005850
Sodium iodide	NaI	0·015002
Hydrochloric acid	HCl	0·003646

Equivalence of Decinormal Ammonium Thiocyanate Solution.

1 c.c. of Solution (containing 8·611 grams per litre) corresponds to

		Gram.
Copper	Cu	0·00636
Silver	Ag	0·010793
Silver nitrate	$AgNO_3$	0·016994

Equivalence of Decinormal Sodium Chloride Solution.

1 c.c. of Solution (5·85 grams per litre) corresponds to

		Gram.
Silver	Ag	0·010893
Silver nitrate	$AgNO_3$	0·016994

Equivalence of Decinormal Iodine Solution.

1 c.c. of Decinormal Iodine (12·697 grams per litre) corresponds to

		Gram.
Arsenious acid	As_2O_3	0·00495
Antimony oxide	Sb_2O_3	0·00721
Bromine (free)	Br	0·007996
Tartar emetic	$K(SbO)C_4H_4O_6+\frac{1}{2}H_2O$	0·016619
Chlorine (free)	Cl	0·003545
Iron	Fe	0·005588
Ferrous oxide	FeO	0·007188
Ferrous carbonate	$FeCO_3$	0·011588
Potassium dichromate	$K_2Cr_2O_7$	0·004909
Potassium permanganate	$KMnO_4$	0·003164
Sodium sulphite, crystals	$Na_2SO_3+7H_2O$	0·012613
Sodium thiosulphate	$Na_2S_2O_3+5H_2O$	0·02483
Sulphuretted hydrogen	H_2S	0·00170
Sulphurous acid	H_2SO_3	0·00410
Sulphur dioxide	SO_2	0·00320
Ferric oxide	Fe_2O_3	0·007988

TABLE OF CONVERSION FACTORS.

To Convert	To	Multiply by
Acres	Hectares	·4047
Atmospheres	Kilos per square cm.	1·033
Atmospheres	Mm. of mercury	760·
Atmospheres	Pounds per square inch	14·7
British Thermal Units	Calories	·252
British Thermal Units	Foot pounds	777·
British Thermal Units	Watt. hours	·293
B.Th.U. per cubic foot	Calories per centimetre	8·90
B.Th.U. per lb.	Calories per kilo	·556
Calories	British Thermal Units	3·97
Calories „	Joules	4180·
Calories per centimetre	B.Th.U. per cubic foot	·1124
Calories per kilo	B.Th.U per lb.	1·800
Centigrade degrees	Fahrenheit degrees	1·8 and add 32
Centimetres	Inches	·394
Cubic centimetres	Cubic inches	·0610
Cubic feet	Cubic metres	·0283
Cubic feet	Gallons	6·25
Cubic feet	Litres	28·33
Cubic inches	Cubic centimetres	16·4
Cubic metres	Cubic feet	35·3
Cubic metres	Cubic yards	1·307
Cubic metres per kilo	Cubic feet per lb.	16·01
Cubic yards	Cubic metres	·765
Feet	Metres	·3048
Fahrenheit degrees	Centigrade degrees	Deduct 32, and $\times \frac{5}{9}$
Foot-pounds	Foot-poundals	32·2
Foot-pounds	Joules	1·356
Foot-pounds	B.Th.U.	·00129
Gallons	Litres	4·546
Gallons	Cubic feet	·160
Grains	Grammes	·0648
Grammes	Grains	15·44
Grammes	Pounds (Av.)	·002205
Grammes per cubic centimetre	Pounds per cubic foot	62·4
Hectares	Acres	2·471
Hectares	Square yards	11,960·
Horse Power	B.Th.U. per second	·707
Horse Power	Calories per second	·178
Horse Power	Kilowatts	·746
Inches	Centimetres	2·54
Inches mercury gauge	Atmospheres	·0333
Inches mercury gauge	Inches water gauge	13·6
Inches mercury gauge	Pounds per square inch	·490
Inches water gauge	Inches mercury gauge	·0735
Inches water gauge	Pounds per square inch	·0360
Joules	Foot-pounds	·738
Joules	Calories	·000239
Kilogrammes	Pounds	2·205
Kilos per square centimetre	Pounds per square inch	14·22
Kilos per square metre	Pounds per square foot	·205
Kilometres	Miles	·6214
Kilometres per hour	Knots	·54
Kilowatts	B.Th.U. per second	·949
Kilowatts	Calories per second	·239

TABLE OF CONVERSION FACTORS—*continued.*

To Convert	To	Multiply by
Kilowatts	Foot-pounds per second	738·
Kilowatts	Horse Power	1·341
Knots	Miles per hour	1·151
Litres	Cubic feet	·0353
Litres	Gallons	·220
Litres	Pints	1·76
Logarithms (Common)	Hyperbolic	2·3026
Logarithms (Hyperbolic)	Common	·4343
Metres	Feet	3·281
Metres	Inches	39·37
Metres	Yards	1·094
Miles	Kilometres	1·609
Miles per hour	Feet per second	1·467
Miles per hour	Knots	·869
Millimetres	Inches	·03937
Ohms per centimetre cube	Ohms per inch cube	·394
Ohms per inch cube	Ohms per cm. cube	2·54
Ounces (Av.)	Grammes	28·35
Ounces (Troy)	Grammes	31·09
Pints	Litres	·568
Pounds (Av.)	Kilogrammes	·454
Pounds per cubic foot	Grammes per c.c.	·016
Pounds per square foot	Kilos per square metre	4·88
Pounds per square inch	Kilogrammes per sq. cm.	·0703
Pounds of water evaporated from and at 212° F.	Kilos of water evaporated from and at 100° C.	·3828
Quarts	Litres	1·136
Radians	Degrees	57·3
Square centimetres	Square inches	·155
Square inches	Square centimetres	6·45
Square feet	Square metres	·093
Square metres	Square feet	10·76
Square metres	Square yards	1·196
Square miles	Square kilometres	2·59
Square yards	Square metres	·836
Tons	Kilogrammes	1015·6
Tons per square inch	Kilos per square cm.	157.5
Tons per square inch	Atmospheres	152·4
Watt-hours	B.Th.U.	3·415
Yards	Metres	·9144

Note.—In the above table the calorie is the kilogramme calorie, sometimes called the "large calorie."

MENSURATION OF SURFACES AND SOLIDS.

Area of a circle = Radius squared × 3·1416.
Volume of a sphere = 1⅓ × 3·1416 × radius cubed.
Volume of a cylinder = Area of a base × height.
Circumference of a circle = 2 × 3·1416 × radius.
Area of sector of circle = Length of area × ½ radius.
Area of a segment of circle = Area of sector less area of triangle.
Area of a square, rhombus or rhomboid = Base × height.
Area of an equilateral triangle = Square of side × 0·433.
Area of trapezium = ½ sum of two parallel sides × height.

Area of regular polygon = Inscribe a circle, then $\frac{1}{2}$ radius of circle, and length of one side × number of side.
Area of an ellipse = Major axis × minor axis × 0·7854.
Surface of cylinder or prism = Area of two ends × length and perimeter.
Surface of cone or pyramid = $\frac{1}{2}$ side × perimeter of base + area of base.
Surface of cube or parallelopipedon = Sum of areas of all the sides.
Surface of sphere = Diameter squared × 3·1416.
Content of prism or cylinder = Area of base × height.
Content of cone or pyramid = $\frac{1}{3}$ (area of base × perpendicular height).
Content of cube or parallelopipedon = Length × breadth × depth.
Content of sphere = Cube of diameter × 0·5236.
Volume of hexagonal = Square of side × 2·598 × height.
Volume of paraboloid = $\frac{1}{2}$ volume of circumscribing cylinder.
Volume of ring (circular section) = Mean diameter of ring × 2·47 × square of diameter of section.

FREEZING MIXTURES.

Freezing mixtures are salts or mixtures of salts which cause a lowering of temperature when dissolved. The lowering of temperature increases with the heat of solution, solubility and concentration of the solution, and is greater the lower the freezing point of the solution, since the freezing point marks the limit of cooling. The mixtures, in order to give satisfactory results, must be used in relatively large amounts, and be cooled as far as possible before use. The solids used should be finely powdered.

A. Mixtures with Water.

Mixture.	*Cooling.*	
	From	To
5 parts ammonium chloride 5 „ potassium nitrate 16 „ water	10°	-17°
5 „ ammonium chloride 5 „ potassium nitrate 8 „ sodium sulphate (cryst.) 16 „ water	10°	-20°
1 part ammonium nitrate 1 „ water	10°	-20°
1 „ ammonium nitrate 1 „ sodium carbonate (cryst.) 1 „ water	10°	-25°
3 parts potassium sulphocyanide 2 „ water	10°	-25°
5 „ calcium chloride (cryst.) 3 „ water	10°	-15°

B. MIXTURES WITH DILUTE ACIDS.

Mixture.	*Cooling.* From	To
3 parts sodium sulphate (cryst.) 2 ,, dil. nitric acid (2 acid, 1 water)	10°	- 20°
6 ,, sodium sulphate (cryst.) 4 ,, ammonium chloride 2 ,, potassium nitrate 4 ,, dil. nitric acid	10°	- 25°
6 ,, sodium sulphate (cryst.) 5 ,, ammonium nitrate 5 ,, dil. nitric acid	10°	- 28°
6 ,, sodium phosphate 4 ,, dil. nitric acid	10°	- 20°
5 ,, sodium sulphate (cryst.) 4 ,, dil. sulphuric acid (1 acid, 1 water)	10°	- 18°
8 ,, sodium sulphate (cryst.) 5 ,, conc. hydrochloric acid	10°	- 22°

C. MIXTURES WITH SNOW OR POWDERED ICE.

Mixture.	From	To
1 part sodium chloride 2 parts snow	0°	- 20°
1 part ammonium chloride 2 parts sodium chloride 5 ,, snow	0°	- 30°
1 part ammonium chloride 2 parts sodium chloride 1 part potassium nitrate 5 parts snow	0°	- 35°
5 ,, sodium chloride 5 ,, ammonium nitrate 12 ,, snow	0°	- 40°
5 ,, calcium chloride (cryst.) 4 ,, snow	0°	- 50°
3 ,, calcium chloride (cryst.) 2 ,, snow	0°	- 35°
5 ,, potassium hydroxide (cryst.) 3 ,, snow	0°	- 35°
1 part sulphuric acid (diluted with 20% of its weight of water) 3 parts snow	7°	- 50°
1 part conc. hydrochloric acid, sp. gr. 1·18 1 ,, snow	0°	- 37°
1 ,, nitric acid 2 parts snow	0°	- 56°

MELTING POINTS. (FREEZING POINTS.)

	Degrees Cent
Alcohol (ethylic)	−130
Aluminium	657
Ammonia	−75
Antimony	630
Asphalt	100
Benzene (pure)	6
Bismuth	268
Boric acid	186
Brass	900
Bromine	−22
Bronze	900
Cadmium	321
Carbon dioxide	−70
Cobalt	1500
Colophonium	135
Copper	1084
Cupric chloride	498
Cuprous chloride	434
Fat, ox	40
,, sheep	42
,, pig	27
Fluorspar	902–1330
Glass	1200
,, containing lead	1000
Gold	1063
Iron, cast, white	1075–1135
,, grey	1200–1250
,, wrought	1500
Iodine	113
Lead	326
,, oxide	954
,, chloride	490
Magnesium	633
Mercury	−39·5
Mercuric chloride	287–293
Naphthalene	79
Nickel	1484
Nitric acid	−54
,, oxide	−148·8 to −167
Nitric tetroxide	−11
Nitrous oxide	−102
Palm oil	29
Paraffin, hard	45–60
Pitch (coal tar, hard)	150–200
Phosphorus	44
Platinum	1710
Potassium chlorate	284–302
,, iodide	614–723
,, carbonate	834–898
,, nitrate	327–353
,, chloride	740–804
,, sulphate	1015–1078

MELTING POINTS. (FREEZING POINTS)—*continued.*

	Degrees Cent.
Rose's metal	94
Selenium	217
Stearic acid	70
Steel	1375
Silver, metallic	961·5
,, chloride	450–460
,, nitrate	217
Strontium chloride	825
Sodium chloride	772–840
,, sulphate	861–884
,, nitrate	308–330
,, chlorate	248–302
,, carbonate	814–918
Spermaceti	45–50
Sulphur (monoclinic)	120·1
,, dioxide	−72·7
,, trioxide	14·8
Sulphuretted hydrogen	−85
Thallium	301
Tin	232
,, tetrachloride	−33
Wax, bees'	62–70
Wood's metal	70
Zinc	419

LINEAR EXPANSION OF SUBSTANCES.

By variation of temperature from 0° *to* 100° C. (32°–212° F.)

Brass	0·001868	1 : 535
Charcoal from oak	0·001200	1 : 833
,, ,, fir	0·00100	1 : 1000
Copper	0·001718	1 : 582
Glass, flint	0·000817	1 : 1219
,, white	0·000861	1 : 1161
,, green	0·000766	1 : 1305
Gold	0·001466	1 : 682
Iron, wrought	0·001235	1 : 812
,, cast	0·001110	1 : 901
Lead	0·002848	1 : 351
Marble of Carrara	0·000849	1 : 1178
,, St. Beat	0·000418	1 : 2392
Platinum	0·000884	1 : 1132
Silver	0·001908	1 : 524
Solder, hard	0·002058	1 : 486
Steel, hardened	0·001240	1 : 807
,, not hardened	0·001079	1 : 927
Tin	0·001938	1 : 516
Water	0·015538	1 : 71·4
Zinc	0·002942	1 : 340

REDUCTION OF WATER PRESSURE TO MERCURIAL PRESSURE.

Aq.	Hg.	Aq.	Hg.	Aq.	Hg.	Aq.	Hg.	Aq.	Hg.
1	0·07	23	1·70	45	3·32	67	4·94	89	6·57
2	0·15	24	1·77	46	3·39	68	5·02	90	6·64
3	0·22	25	1·84	47	3·47	69	5·09	91	6·72
4	0·30	26	1·92	48	3·54	70	5·17	92	6·79
5	0·37	27	1·98	49	3·62	71	5·24	93	6·86
6	0·44	28	2·07	50	3·69	72	5·31	94	6·94
7	0·52	29	2·14	51	3·76	73	5·39	95	7·01
8	0·59	30	2·21	52	3·84	74	5·46	96	7·08
9	0·66	31	2·29	53	3·91	75	5·54	97	7·16
10	0·74	32	2·36	54	3·99	76	5·61	98	7·23
11	0·81	33	2·44	55	4·06	77	5·68	99	7·31
12	0·89	34	2·51	56	4·13	78	5·76	100	7·38
13	0·96	35	2·58	57	4·21	79	5·83	200	14·76
14	1·03	36	2·66	58	4·28	80	5·90	300	22·14
15	1·12	37	2·73	59	4·35	81	5·98	400	29·52
16	1·18	38	2·80	60	4·43	82	6·05	500	36·90
17	1·26	39	2·88	61	4·50	83	6·13	600	44·28
18	1·33	40¾	2·95	62	4·58	84	6·20	700	51·66
19	1·40	41	3·03	63	4·65	85	6·27	800	59·04
20	1·38	42	3·10	64	4·72	86	6·35	900	66·42
21	1·55	43	3·17	65	4·80	87	6·42	1000	73·80
22	1·62	44	3·25	66	4·87	88	6·49		

SPECIFIC GRAVITY AND PERCENTAGE OF SATURATED SOLUTIONS.

The percentage refers to Anhydrous Salt.

	Temperature.	Percentage of Salt.	Specific Gravity.	Degrees Twaddell.
Ammonium chloride	15	26·30	1·0776	15·5
,, sulphate	19	50·00	1·2890	57·8
Barium chloride	15	25·97	1·2827	56·5
Calcium chloride	15	40·66	1·4110	82·2
Magnesium sulphate	15	25·25	1·2880	57·6
Potassium chloride	15	24·90	1·1723	34·4
,, carbonate	15	52·02	1·5708	114
,, nitrate	15	21·07	1·1441	28·8
,, sulphate	15	9·92	1·0831	16·6
Sodium chloride	15	26·395	1·2043	40·8
,, carbonate	15	14·35	1·1535	30·7
,, nitrate	19·5	46·25	1·3804	76
,, sulphate	15·0	11·95	1·1117	22·3

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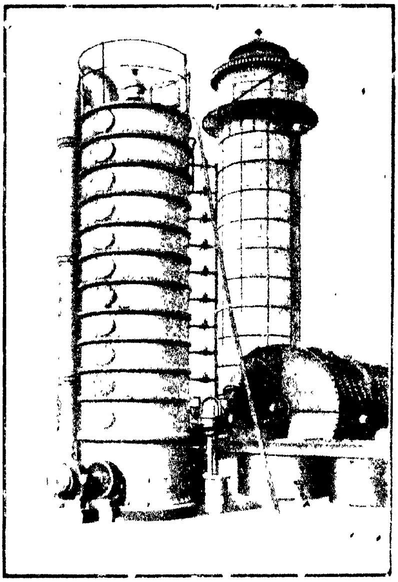

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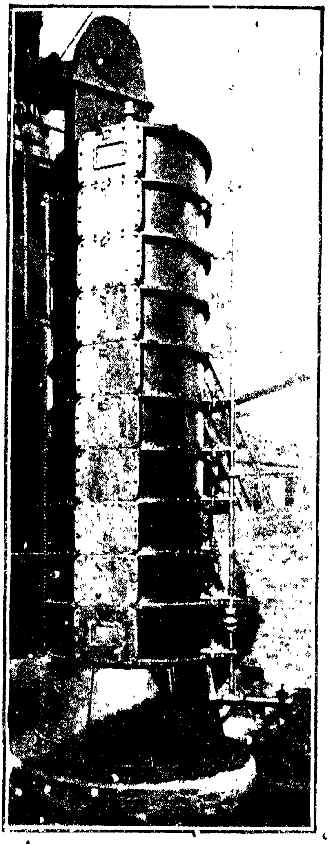

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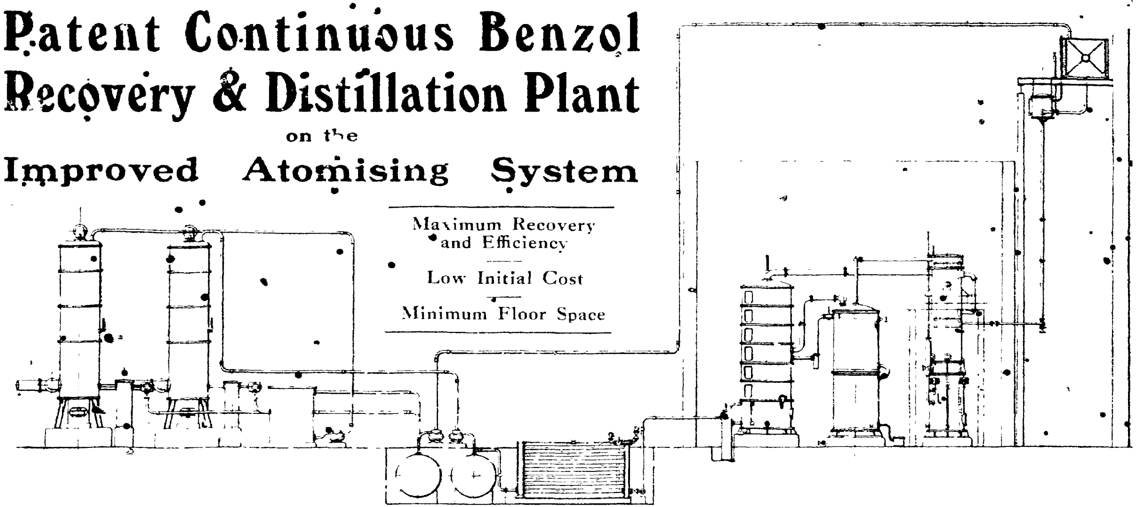

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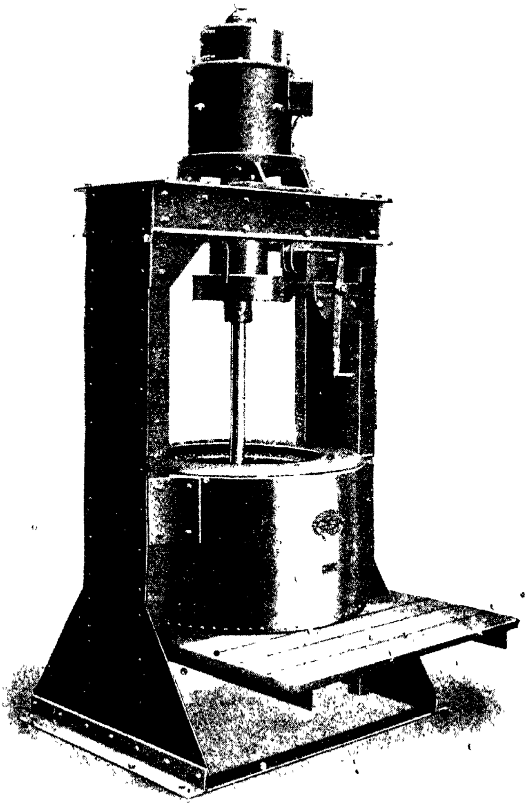

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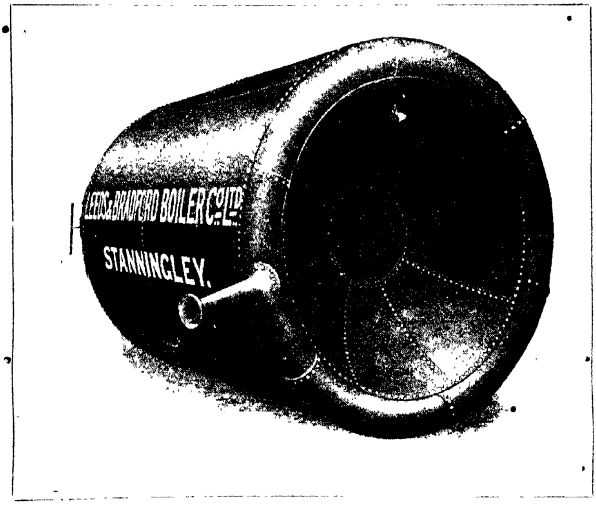

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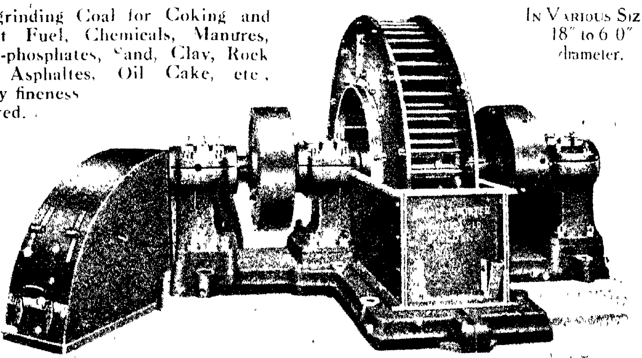

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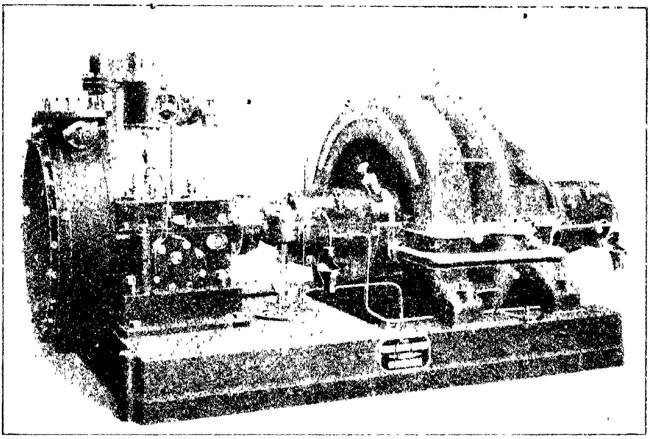

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